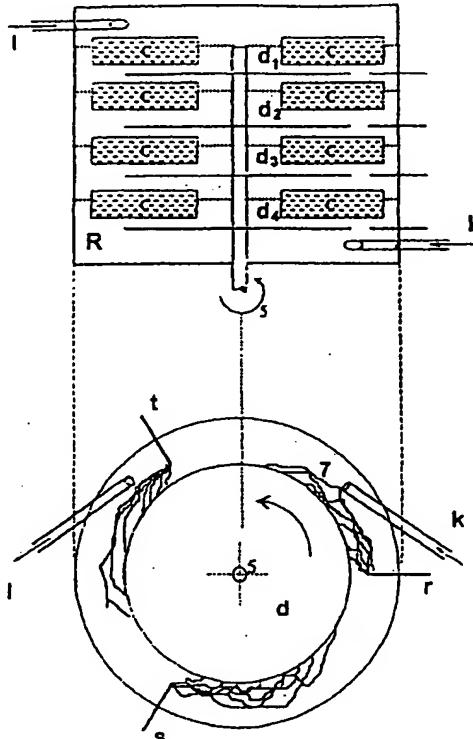


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(54) Title: DEVICE WITH PLASMA FROM MOBILE ELECTRIC DISCHARGES AND ITS APPLICATIONS TO CONVERT CARBON MATTER		
(57) Abstract		
A process and system for using plasma from mobile electric discharges for conversion of a carbon substance. The process and system (R) use plasma from mobile electric discharges (7) for conversion of carbon substances, such as light hydrocarbons, heavy hydrocarbons or residues from refining these, CO ₂ or CO into products such as gases containing CO and/or H ₂ and/or C ₂ H ₄ and C ₂ H ₂ and/or liquid carbon fuels. The conversions are based on oxidation and/or cracking of the matter in the presence of water vapor and of gas such as CO ₂ , O ₂ , N ₂ , H ₂ , alone or mixed. The system generates a non-equilibrium plasma by very rapidly stretching the discharges (7) established between at least one fixed electrode (r, s, t) and at least one mobile electrode (d). The non-equilibrium plasma sweeps the gas passing through the reactor in order to stimulate chemical conversions. The flow of the matter activated by the plasma entering through (k) may pass through one or more discharge stages (d ₁ , d ₂ , d ₃ , d ₄) and may be brought into contact with a metal or ceramic body placed near the discharges before exiting through (1). This body becomes active in the presence of the catalytic species originating from the plasma and thus participates in the continuation of the conversion.		

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TITLE: DEVICE WITH PLASMA FROM MOBILE ELECTRIC DISCHARGES AND ITS APPLICATIONS TO CONVERT CARBON MATTER**BACKGROUND OF THE INVENTION**

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1. Field of the Invention

The invention relates generally to the conversion of carbon substances and more particularly to the use of fixed and mobile electrodes to stretch discharges and create an off equilibrium plasma for stimulating conversion reactions.

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2. Description of Related Art

The production of synthesis gas starting from light hydrocarbons (HCs) is a very well-known and very important stage, especially for upgrading natural gases and biogases (mixtures with mainly almost equal contents of methane and carbon dioxide) originating from anaerobic fermentation of an organic substance. The chemical upgrading of enormous natural gas (NG) resources may happen to be a much more attractive way than its total combustion limited to direct recovery of energy in ovens, boilers or turbines. Situations also occur in which NGs with high HC content are released into the atmosphere without any recovery of energy; examples of this are found in the oilfield flares which burn a so-called "associated" hydrocarbon gas or the emissions of biogas. Any emission of a uselessly burned (and especially not burned) HC contributes heavily to air pollution.

20 The process most often used now to produce synthesis gas, catalytic steam reforming (or "steam reforming") encounters major problems. In principle, it needs only high temperature (thermodynamic reason) and high pressure (kinetic reason). However, in practice, despite the know-how for the production of SG according to this process, mastering the combination of composition, pressure and temperature is difficult, even impossible without resorting to catalysts. In order to reform NG with steam, usually a catalyst is used: presence of a solid substance in 25 highly dispersed and active form (with a specific surface area of at least approximately one hundred square meters per gram) for temperatures which can be reached without too many problems. The traditional steam reforming technology uses ovens in which several hundred fragile metal pipes are located (filled with a catalyst and with a length which may attain several tens of meters), heated externally to the NG. Hence, the large quantities of carbon dioxide originating from the combustion are ejected into the atmosphere by these ovens with a very poor thermal 30 yield. Moreover, this technology is tied to very high pressure losses. The temperature which can be withstood by the oven pipes prevents also a decrease in CO₂ content in the SG itself (CO₂ is a hindrance product originating from a parasite reaction at too low a temperature). Other problems are tied to catalyst poisoning by sulfur and/or nitrogen, aging the catalysts, the necessary excess of steam and/or the formation of soot (which blocks the entire tubular system at macroscopic scale and, above all, the microscopic pores of the catalyst). These problems are observed 35 mostly at the time of steam reforming of heavier HCs (heavier than methane) which are more fragile and, therefore, more coking.

Dry reforming of HCs with carbon dioxide is not yet used industrially, since it requires the presence of catalysts capable of withstanding high temperatures in a highly coking medium. Research is still actively pursued, since this reforming would have important applications to produce a CO rich SG, for example for "oxo" syntheses, 40 starting from NGs (or biogases) with high CO₂ content and, for this reason, considered less valuable.

Partial oxidation (reaction 6 or 6a) is sometimes achieved industrially but it requires always special care to prevent explosion of a reactor when the O₂/NG ratio is exceeded. We will see that this risk disappears in the presence of our mobile electric discharges always present in the reactive medium.

5

SUMMARY OF THE INVENTION

Broadly speaking, the invention comprises a method and system for converting carbon substances in plasma-chemical reactors based on mobile electric discharges. The discharges cause high activation of the medium by unusual species (with respect to the traditional conditions of conversions) originating from the matter in which these discharges develop. Thus, electrons, atoms, ions and molecular radicals such as H, OH, O, O₂, H⁺, O⁺, O₂⁺, O₂, HO₂, CH₃, CH₂, CH, C₂ and many others are detected. Most of these species may exist in their electronic or vibratory excited states with a rather long lifetime. They are also known to be extremely chemically active.

In one embodiment, a device comprises one or more fixed electrodes and one or more mobile electrodes. Discharges established between the fixed electrodes and the mobile electrodes generate an off equilibrium plasma by very rapidly stretching the discharges between the electrodes and thereby causing the off equilibrium plasma to sweep the gas passing through the reactor in order to stimulate chemical conversions. The flow of the matter activated by the plasma may be brought into contact with a metal or ceramic body placed near discharges. This body becomes active in the presence of the catalytic species originating from the plasma and thus participates in the continuation of the conversion.

20

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and advantages of the invention will become apparent upon reading the following detailed description and upon reference to the accompanying drawings in which:

Fig. 1 is an illustration of a toothed mobile electrode used in one embodiment.

Fig. 2 is an illustration of a multiple-stage reactor using mobile disk electrodes.

25 Fig. 3 is an illustration of a mobile electrode comprising a circular brush.

Fig. 4a is an illustration of an embodiment using an inductor to alter the phase of the terminal voltage with respect to the discharge current and voltage.

Fig. 4b is a graph of the terminal voltage, discharge current and discharge voltage for the embodiment illustrated in Fig. 4a.

30 While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and will herein be described in detail. It should be understood, however, that the drawing and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

35

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The system described herein proposes a device with high voltage mobile discharges, as well as its application for the conversion of hydrocarbons and/or carbon dioxide and/or carbon monoxide.

40 We propose first an endothermic process with upgrading conversion of light hydrocarbons (HCs) aided by a specific plasma generated in a device with mobile electric discharges in the presence of carbon dioxide CO₂ or steam

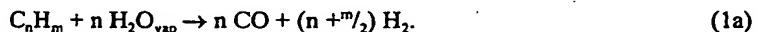
or of an H₂O/CO₂ mixture. We can also add to the HC load an amount of oxygen (either pure or contained in the air or in any mixture) in order to obtain partial oxidation of the feed. The processes are illustrated by the conversion of natural gas (NG) containing mostly methane, but also some ethane, propane and butanes. The process can thus be applied to any pure HC, such as CH₄, C₂H₆, C₃H₈ or C₄H₁₀, as well as to their mixtures of natural or industrial origin.

5 In the presence of steam, we convert CH₄ (and other light HCs) into "synthesis gas" (SG) consisting mostly of hydrogen and of carbon monoxide CO and also of other valuable products, such as ethylene C₂H₄ and acetylene C₂H₂, without using traditional catalysts. The process is based mainly on steam reforming reactions, such as:



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knowing that the heavier hydrocarbons C_nH_m will undergo similar steam reforming:



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We observe, at the same time, methane cracking according to the following reactions:



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and similar cracking of heavier HCs yielding acetylene, ethylene, propylene C₃H₆ and other unsaturated olefinic and/or acetylenic HCs. Also, part of the CO produced undergoes a slightly exothermal conversion called "water shift":

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Thus, at the time of said steam reforming of a NG or of another HC mixture, we produce a SG containing all these gases produced by reaction (1) through (3), in unusual ratios with respect to the conventional methods of production of a "classic" SG.

30

We propose then "dry" reforming of the NG (or of another HC mixture) with carbon dioxide according to the following reaction:



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knowing that other C_nH_m hydrocarbons react in a similar manner:



and that said conversion is accompanied by cracking reactions, such as (2), (2a) and (2b). At the same time, we also observe a conversion called "inverse water shift":



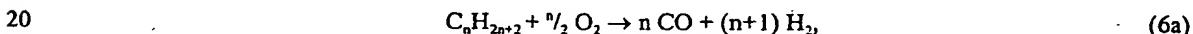
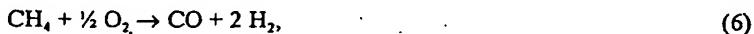
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following the appearance of the hydrogen (reactions 4 and 4a) in the mixture containing CO_2 which has not yet reacted. Thus, at the time of said dry reforming of a NG or of another HC mixture or even of a biogas (mixture of CH_4 with CO_2) we produce a SG containing all the above-mentioned molecules.

Obviously, we can mix the two oxidizers, H_2O and CO_2 , in any ratios and make them react with a NG or 10 another mixture of HCs, in order to perform a "mixed" conversion based simultaneously on the previously mentioned reactions, each of these reactions being weighted according to the specification of the product desired and as a function of the load to be converted.

Reaction (4) or (4a) of the "dry" reforming can also be considered as an upgrading conversion of CO_2 , a gas suspected of causing the greenhouse effect; of course, that will depend on the main objective of the industrial 15 operation considered.

In the presence of elemental oxygen, we observe weakly exothermal reactions of partial oxidation of the methane and/or of its paraffinic homologues:



as well as methane dimerization:



Partial oxidation of very heavy HCs can also be carried out in order to convert them to lighter liquid hydrocarbons. Therefore, this would consist of slightly oxidizing cracking with high added value.

In the presence of mobile electric discharges, we observe also all the other conversions described by equations (1) through (7) and also a complete parasite combustion and highly exothermal reaction:

30



However, this reaction is minor, since its products are to a large extent consumed by profitable reactions (1) or (1a) and (4) or (4a) or neutral reactions (3) and/or (5).

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Nothing prevents partial oxidation (6) or (6a) in the presence of steam and/or carbon dioxide already present in the feed or added, in order to proceed with a $\text{O}_2/\text{H}_2\text{O}$ or O_2/CO_2 or even $\text{O}_2/\text{H}_2\text{O}/\text{CO}_2$ hybrid conversion, so as to obtain a SG with a special composition or to upgrade a particular feed of HCs.

Other applications are noted when the values of the oxidizer/HC ratios are extreme. This is the case of a NG or of another HC mixture without oxidizer or, on the contrary, of CO or CO₂, in the absence of an "organic" reactant such as CH₄, NG or other HC mixture. In these cases, we aim at:

- The special conversions described by reactions (2), (2a), (2b) and similar reactions with partial cracking of a NG or of an HC, possibly diluted in a neutral gas or in the hydrogen, to obtain one or more products among those written on the right side of reactions (2), (2a), (2b) and similar reactions;
- The "water shift" described by reaction (3) in order to obtain hydrogen starting from carbon monoxide;
- The "inverse water shift" (5) to convert carbon dioxide to carbon monoxide.

All the above-mentioned conversions are performed in plasma-chemical reactors based on mobile electric discharges, called GlidArc-II, which are the subject of this application. These discharges cause high activation of the medium by unusual species (with respect to the traditional conditions of conversions) originating from the matter in which these discharges develop. Thus, electrons, as well as atoms, ions and molecular radicals are detected, such as: H, OH, O, O₂, H⁺, O⁺, O₂⁺, O₂⁻, HO₂, CH₃, CH₂, CH, C₂ and many others. Most of these species may exist in their electronic or vibratory excited states with a rather long lifetime. They are also known to be extremely chemically active.

HC conversion according to endothermic reactions (1) through (2b) and (4) through (5) would require a supply of preferably "clean" energy, not connected with any external combustion which is not economic and is highly polluting. The best way to help these reactions would be to have electric arcs and/or discharges directly in the medium to be converted, imposing permanent distribution of energy in the larger volume to be treated. The transfer of energy of electric origin to the gas mixture would occur by direct transfer of the energy to the molecules. This would entail excitation, ionization and dissociation phenomena and also Joule effect, considering the mixture partially ionized as a gaseous electric conductor. The gas mixture having become a conductor after ionization (itself due to dielectric breakdown, hence to pre-ionization) between electrodes brought to different potentials, would be considered as an electric resistance and, at the same time, as a sort of electrolyte in gaseous phase: the plasma.

The weakly exothermic reactions (3) and (6) to (7) develop better at higher temperatures because of a merely kinetic reason. The presence of a traditional catalyst or of catalytic species in homogeneous phase helps greatly in this type of reactions. Such species are obviously present in a plasma.

Plasma is defined as a state of matter and, therefore, cannot be taken as a criterion of similarity for different, previously known processes. There is a multitude of plasmas and several ways whereby to obtain each of these plasmas. By definition, plasma is a gaseous medium in which particles are partially oxidized. In most plasmas, the main physical macroscopic quantity - temperature - is the same for all the components: this is thermodynamic equilibrium. These conditions can be easily obtained: it is sufficient to supply much energy, such as in the case of plasma torches ("plasmatrons") in which plasma is produced by a very high current electric arc. There are other devices capable of generating this state, such as induction or radiofrequency (RF) torches in which the gas medium becomes resonant with a very high frequency electromagnetic field. These plasmas are called "thermal plasmas". It is obvious that a thermal plasma will modify the chemistry of a gas mixture by destroying almost all the molecules, especially the fragile ones, such as HCs. The fragments which meet at the end of the process, after a sudden drop in temperature produced by quenching without recovery of energy, originate from partial recombination phenomena

producing simple molecules. This chemistry offers mediocre prospects; it is energy costly and presents problems connected with the high temperature, such as the resistance of the materials.

Chemists prefer plasmas which do not respect the thermodynamic equilibrium conditions. For example, it is sufficient to act on the free electrons. It is also possible to act on the rotation or vibration properties of certain molecules. In terms of energy, that breaks again the balance of energy exchange between the plasma and the medium surrounding it. This state is called "out of thermodynamic equilibrium" or simply "non-equilibrium". These plasmas are sometimes called "low temperature" plasmas, although the concept of temperature can no longer be used! There are several methods for generating these plasmas: microwaves, electron beams, flame fronts, etc. However, at industrial scale, the generators of such transposable plasmas are rare and fit only a well-defined application. This is the reason why these plasmas are not used much in chemistry.

Furthermore, when a plasma is prepared or its existence is ended, the equilibrium is broken. These transitory states are in fact non-equilibrium plasmas and last only a few milliseconds. A type of plasma already makes use of this phenomenon, the plasma from gliding electric arcs "GlidArc-I" (see further on). Apart from the numerous geometric possibilities of such a plasma generator and, very globally, the parameters on which a chemist can act are: pressure, temperature, gas speed, current intensity, voltage and electric frequency. Such a number of parameters exceeds the conventional reasoning capabilities of the expert. For each application, real know-how and inventive activity are necessary to attain results in which the objectives are economic feasibility and respect of ecological principles. GlidArc-I already enabled a chemist to envision the distribution of an energy supply directly in the gas mixture, without, for example, resorting to catalysts. A chemist could also distribute the energy directly rather than in thermal form or in chemical form. He could also intervene on the flow still charged with active species from the arc or discharge zone to have these substances react with the feed to be converted or reconverted in a post-plasma zone. Nevertheless, some difficulties were determined in the last few years, hence our research to bypass them. Thus, we have succeeded in perfecting a totally new device with mobile arcs, GlidArc-II.

Various electric plasma devices have already been tested as source of an "active" energy. Our bibliographic search concerning the last three decades provides few published or patented results concerning the conversion of hydrocarbons assisted by plasma (outside of our own work). The main cause of these problems is connected to the presence of oxygen (elementary oxygen or oxygen deriving from dissociation of the H₂O and/or CO₂ molecules) attacking the conventional tungsten or graphite electrodes of traditional plasma devices. However, we will report these attempts at using different plasma generators. Systematically, both the basis and the reaction process are different from ours; there is only one common point: the use of the very broad term "plasma" or the possibility of handling the same hydrocarbon molecules.

K. KARL et al. [Verfahren zur Herstellung eines wasserstoffreichen Gases aus Kohlen-wasserstoffen, CH 378 296 (1957)] propose steam reforming of hydrocarbons under 66.7 kPa to 0.3 MPa pressure in a "silent" discharge characterized by a very intense 0.3 to 0.5 MV/m electric field. This source of plasma has been known for a century; it is totally different from that which is the subject of this application.

R.J. HEASON presented in 1964 his doctorate thesis concerning pyrolysis of methane as well as the reaction of CH₄ with steam in an arc plasma (700 A, 20 V) in argon. These results were published in manuscript form ["Investigation of methane and methane-stem reactions in an argon plasma", Dissertation, Ohio State Univ., Columbus]. This is a "thermal" plasma and a device consuming a large quantity of argon (2 moles Ar for 1 mole CH₄).

C.H. LEIGH and E.A. DANCY ["Study on natural gas reforming by plasma arc"; Proc. of the Int. Round Table on Study and Appl. of Transport Phenomena in Thermal Plasmas, contribution I.5, Odeillo, 1975, 11 pp.] heated a mixture of CO₂/CH₄ ~ 1 in a jet of argon plasma at the outlet of a traditional arc plasmatron. The temperature of the jet was approximately 10 kK. The argon flow was in the same order of magnitude as that of the mixture to be treated. These researchers observed a conversion of 11 to 74% carbon to H₂, CO, C₂H₄ and C₂H₆ (without ever detecting C₂H₂ or H₂O in the products!?). No application was possible because of the high consumption of electric energy (70% of this energy went to the water cooling the plasmatron) as well as the use of the noble gas.

P. CAPEZZUTO et al. ["The oxidation of methane with carbon dioxide, water vapor and oxygen in radio-frequency discharges at moderate pressures", 3rd Int. Symp. on Plasma Chemistry, Limoges, 1976, contribution G.5.11, 7 pp.] also studied partial oxidation of methane separately mixed with CO₂ or with O₂ or with H₂O with oxidizer/CH₄ ratios = 1. The 35 MHz radiofrequency (RF) plasma reactors needed an additional argon flow and could operate only at low pressures around 2.7 kPa. For the total input gas flow rate of 3 to 36 l(n)/min (the "n" indicating the gas volume at normal condition of 0°C and 1 atm) the energy density at the range of 1 to 12 kWh/m³(n) was very big. No industrial application was possible because of the high consumption of electric energy and of noble gas (in addition to complexity of electric supply and the need to work under vacuum). The mechanical setup constraints, the low energy yield and the insufficient unit powers of the RF plasma sources cause the use of this method to be poorly adapted from the economic point of view to conversions of large volumes of gas. Nevertheless, it is of interest to note that, in any case, the authors observe an almost total conversion of the methane and the appearance of the following products:

- mainly H₂, CO, C₂H₂ with presence of C₂H₄ (< 5%) and of C₂H₆ (< 1%) for the CO₂/CH₄ system,
- the same as those above but with some traces of CO₂ for the H₂O/CH₄ system.

A patent of S. SANTEN et al. ["Thermal reforming of gaseous hydrocarbon" GB-A-2172011 (1986)] claims the use of a plasma generator to heat reagents (a gaseous hydrocarbon, some water vapor and possibly some coal), entirely or partially, up to a temperature exceeding 1200°C. At such temperatures, these inventors expect favorable conditions to handle their process merely thermally, without the use of catalysts. The temperatures reached in the reactor and the thermal manner of the reforming (claimed and even emphasized in the patent title) therefore indicate treatment of hydrocarbons under thermodynamic equilibrium. The process is based on a direct arc plasma generator (two annular electrodes) or transferred arc plasma generator, which are very traditional devices that have been known for nearly a century!

L. KERKER wrote in general on production tests of synthesis gas at Huls [Herstellung von Reduktionsgas oder Synthesegas mit Lichtbogenplasmaverfahren", Elektro-wärme international B, Industrielle Elektrowärme, vol. 45 (3-4), 155-61 (1987)]. The illustrations indicate a very powerful (1 through 9 MW) traditional tubular arc reactor used at this plant since 1939 to produce acetylene. This time, a natural gas steam reforming project is involved, to produce 99.9% pure hydrogen at a very competitive cost with respect to electrolysis (but still more expensive than for hydrogen from traditional steam reforming or partial oxidation methods).

We have also worked since 1986 on the conversion of NGs in thermal plasma reactors. These simple or transferred arc plasma torches make it possible to obtain small volume plasmas at very high temperatures (T > 10 kK). Although these devices represent potential sources of active species, they are nevertheless poorly suitable for chemical applications requiring much lower temperatures, in order not to demolish the hydrocarbon molecules to soot) and mostly larger volumes, filled with plasma, in order to act intimately on the entire fluid to be treated. The

plasma torch technology, for example well established in the area of projection of solids, was found then to be at the same time very expensive and very difficult to implement for chemical processes. However, we have obtained improvements in the area of thermal plasmas in the case of conversion of methane in a specifically controlled electric arc, see P. JORGENSEN et al., "Process for the Production of Reactive Gases Rich in Hydrogen and Carbon Oxide in an Electric Post-Arc, BF 2593493 (1986). However, the structure of the device utilized at the time did not make it possible to use steam as reagent, nor to work without consuming the argon necessary to form a first pilot arc. Later we used almost the same arc with very high current (20 - 150 A) to study ethane oxidation, see K. MEGUERNES et al., "Oxidation of ethane C₂H₆ by CO₂ or O₂ in an electric arc", J. High Temp. Chem. Process., vol. 1(3), p. 71-76 (1992), without much improvement in the consumption of electric energy and of argon.

It is in order to correct these problems that we studied pure methane reforming by carbon dioxide in an electro-reactor which had just been invented by our team, see H. LESUEUR et al., Low Temperature Plasma Generation Device by Formation of Sliding Electric Discharges, BF 2639172 (1988). It consisted of three fixed electrodes between which gliding arcs developed; the plasma medium thus obtained was greatly out of thermodynamic equilibrium and contained numerous excited species which made it highly reactive. This plasma device is currently known under the name of GlidArc-I. Our first tests for the production of synthesis gas starting from a CH₄ + CO₂ mixture directly injected into this new type of plasma (without any cooling nor plasma-forming argon) were reported by H. LESUEUR et al., "Production of synthesis gas (CO + H₂) starting from the oxidation of CH₄ by CO₂ in an electro-reactor with gliding discharges", Physics Colloquium, Supplement to the Journal of Physics, vol. 51 (18), p. C5-49 - C5-56 (1990). We then made a more systematic comparison of methane reforming with carbon dioxide in a transferred arc and in GlidArc-I, to show the great superiority of the gliding arc reactors, see K. MEGUERNES et al., "Oxidation of CH₄ by CO₂ in an electric arc and in a cool discharge", 11th Int. Symp. on Plasma Chem., Loughborough (England), 1993, vol. 2, p. 710-715. Lastly, a complete article on the conversion of CH₄ by CO₂ was published by H. LESUEUR et al., "Electrically assisted partial oxidation of methane", Int. J. Hydrogen Energy, vol. 19(2), p. 139-144 (1994).

This methane reforming by CO₂ shows a very interesting way of upgrading some gases with large contents of carbon dioxide. However, the products from our reactor had a limited H₂/CO molar ratio, between 0.5 and 0.8, almost in agreement with reaction (4). Therefore, this gas composition was totally unsuitable for the Fischer-Tropsch (FT, synthesis of hydrocarbon synthetic fuels, "syncrude") or a similar technology for the production of methanol. The two processes require a synthesis gas with a H₂/CO ratio close to 2.

We then discovered that GlidArc-I is very well suited for a supply of steam as sole plasma-forming medium. The tests on overheating water vapor by this device were performed at on a laboratory scale and at atmospheric pressure. This reactor was supplied with very humid water vapor at 105°C. No deterioration of the plasma generator supplied with water vapor was detected after lengthy experiments. The water vapor, thus overheated at atmospheric pressure and chemically activated by the presence of H, O, OH and other metastable species may be of interest for drying or for chemical conversions, see P. CZERNICHOWSKI and A. CZERNICHOWSKI, Gliding electric arcs to overheat water vapor, 9th Colloquium Université-Industrie "Technical techniques and drying quality", Bordeaux-Talence, 1994, p. B1-1 - B1-7.

It is at this stage that we thought that traditional steam reforming of pure methane could be improved in the presence of gliding electric discharges which provide the reactional medium at the same time with an easily controlled enthalpy and very reactive species. These special discharges and arcs may thus play a catalyst role in

homogeneous phase, see A. CZERNICHOWSKI et al., "Assistance device and process by plasma in non-catalytic steam cracking of hydrocarbon and halogen-organic compounds", BF 2724806 (1994).

The decomposition of CH₄ in the presence of overheated water vapor in a simple GlidArc-I reactor has actually given large quantities (in terms of percentages by volume) of H₂ (up to 66%) and CO (up to 15%). In all cases, we had H₂/CO molar ratios exceeding a value of 4 and even up to 5.8! Moreover, the energy cost (EC) to be borne in order to produce 1 m³(n) of said SG was rather high and another negative point appeared: too large a quantity of unconverted methane remained in the product.

Therefore, we had a new idea, which is the subject of this application: to apply at the same time H₂O and O₂ mixed, so as to perform, at the same time, during one operation in the new reactor with mobile discharges, a conversion of certain HC by endothermic steam reforming (reactions 1 or 1a) and partial oxidation with oxygen (reactions 6 or 6a), which would both contribute part of the energy necessary for the endothermic steam reforming. Part of the oxygen would be consumed by reaction (8), apparently parasitic (but highly exothermic); on the other hand, the CO₂ produced by this reaction could contribute to lower the H₂/CO ratio via reaction (5). This makes it possible to obtain a synthesis gas with an H₂/CO ratio for further use of the SG, for example a FT process. This objective was achieved and, in addition, we were surprised by the appearance of other feed conversion products following reactions (2) through (2b): C₂H₄ and C₂H₂ in relatively high contents. Therefore, these unsaturated products can supply an additional value to this HC conversion process, assisted by the mobile electric discharges. For example, mixed with the synthesis gas, these unsaturated molecules facilitate the construction of hydrocarbon chains at the time of the FT synthesis, see A.L. LAPIDUS et al., Hydrocarbon Syntheses from acetylene-containing gases, Khim. Tverd. Topl. (Moscow), No. 6, p. 3-17 (1996). Thus, formed simultaneously with CO and H₂, during the conversion of hydrocarbons in GlidArc-II, these unsaturated molecules can contribute to direct application of an improved synthesis of liquid hydrocarbons.

A similar approach of O₂/H₂O NG reforming is known in the industry under the name of "Auto-Thermal Reforming" (or the "auto-thermal process"), but this mixed process is obligatorily coupled with post-treatment of the gases leaving the partial combustion zone by means of a traditional catalyst, see T.S. CHRISTENSEN and L.I. PRIMDAHL, "Improve syngas production using autothermal reforming", Hydrocarbon Processing, vol. 73(3), p. 39-46 (1994). A very sophisticated thermal burner is at the core of the process, since all the safety of the operations on the oxygen and HC mixtures at explosion limit depend on proper operation of said burner. Moreover, the high presence of unsaturated HC was not observed there.

We previously mentioned the possibility of converting CO into H₂ or, inversely, H₂ into CO via the so-called "shift" reactions (3) and (5). This makes it possible to prepare mixtures with the desired composition of synthesis gas for a particular application. However, in industrial practice, these reactions require a separate reactor, presence of catalysts and present all the problems of complexity, poisoning and aging of the catalytic load, etc. In order to explain the observed phenomenon of too high an H₂/CO ratio in our pure methane steam cracking tests assisted by GlidArc-I plasma, we performed a series of tests, see A. CZERNICHOWSKI and K. MEGUERNES, "Electrically assisted water shift reaction", 12th Int. Symp. on Plasma Chem., Minneapolis, Minnesota, 1995, vol. 2, p. 729-33. By injecting a mixture of carbon monoxide with steam in GlidArc-I, we clearly observed reaction (3), and this without the least presence of traditional catalyst. Therefore, it is the plasma itself that catalyzed this shift, converting CO into H₂! The same shift can be obtained, in a yet much more advantageous manner, in the GlidArc-II device, (see further on). Moreover, injecting the CO₂ + H₂ mixtures in the GlidArc-II reactor with mobile discharges,

we performed the inverse shift reaction (5) which can serve as a new process for the production of CO from carbon dioxide.

We have already implemented an idea, see P. CZERNICHOWSKI, A. CZERNICHOWSKI, Conversion of hydrocarbons assisted by gliding electric arcs in the presence of steam and/or carbon dioxide, BF 2758317 (1997),
5 which consists of applying H₂O and/or CO₂ and/or a mixture of H₂O/CO₂ (in variable composition, as needed) in order to attain the following in an improved GlidArc-I reactor:

- conversion of some HC by steam reforming (reaction 1 or 1a),
- HC reforming with carbon dioxide (reaction 4 or 4a),
- one single simultaneous HC conversion operation by steam reforming accompanied by reforming with carbon dioxide, in the presence of the inverse shift of part of the hydrogen (reaction 5).

10

Thus, we were able to obtain a synthesis gas having an H₂/CO molar ratio desirable for further utilization of this synthesis gas, for example via a FT process. We were also surprised by the appearance of other conversion products of the load: C₂H₄, C₂H₂ and C₃H₆, in relatively high percentages. These unsaturated products can also contribute additional value to the hydrocarbon conversion processes assisted by electric arcs. The GlidArc-I reactor
15 was divided into two compartments by a diaphragm to reinforce recirculation of the reagents in the arc compartment and to produce maturation in the other empty compartment where the reactions generated in the arc zone can be terminated. The two parts of the GlidArc-I reactor communicated by means of a very large hole allowing the reagents and the active species to penetrate the maturation post-plasma zone.

The beneficial effect for a plasma-chemical conversion of "cold" electric discharges (we also call these
20 "arcs" for currents greater than 5A) was then demonstrated in the GlidArc-I generator of non-equilibrium plasma (previously mentioned) to treat high volumes of gas circulating at very high speed in the vicinity of a system of stationary electrodes. The gas must move in the vicinity of the stationary electrodes in order to drive the bases of the discharges at a local 10 m/s minimum speed. Hence, only a small part of the volume of the gas to be processed was coming in contact with the active species produced in the discharge. The yield from the operation suffered from this.
25 It was also observed that it is very difficult to develop more than 5 kW per pair of electrodes. Consequently, in order to process a large volume of gas, it would be necessary to arrange in battery a large number of modules, each accompanied by a gas acceleration system in the vicinity of the electrodes, which would make the facility very complex. Taking these problems into account, we visualized a new device, described hereinbelow, with electric discharges gliding on mobile electrodes.

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PLASMA DEVICE

The new device, named GlidArc-II, is based on electric discharges which explode on at least two electrodes, of which at least one is mobile. The electrodes are arranged so as to form a mobile structure which can be divergent, but this arrangement is only optional. The gas circulates almost independently with respect to the structure of the
35 electrodes, for example along one of the electrodes, or perpendicular to the movement of the mobile electrode, or also otherwise. The gas flow can also participate in the displacement of the roots of the discharge which, for example, moves rapidly along one of the electrodes. The electrodes involved are anywhere at a minimum distance, regardless of their geometric arrangement. That is where electric breakdown occurs, if the voltage applied to the electrodes exceeds the dielectric breakdown. Immediately after this breakdown, a small volume of plasma, formed between the
40 electrodes, is driven by the movement of one electrode with respect to the other. This driving is possibly aided by a

gas flow. The displacement speed of the discharge depends mostly on the mechanical displacement speed of one (or two) electrode(s). The column of plasma begins to stretch and, at the same time, the voltage at the electrodes increases. During this initial phase, the discharge is near thermodynamic equilibrium, i.e. at each point of the plasma, the temperature of the electrons T_e is near the temperature of the gas T_0 . This regime is caused by the high frequency 5 of collisions between electrons and molecules, as well as by the electric power supplied per unit of length of the discharge, this being sufficient to compensate for the radial losses due to thermal conduction. This equilibrium phase continues as the discharge continues to lengthen, until the moment at which the current attains its maximum value. Starting from this moment, the dissipated electric power decreases, while the losses by thermal conduction continue 10 to increase. Then the discharge enters its thermal non-equilibrium phase and a major drop in the gas temperature T_0 is observed. Instead, the temperature of the electrons is still very high. Due to the drop of the gas temperature T_0 , the heat losses decrease, the length of the off equilibrium plasma can then continue to grow until the moment at which the heat losses become greater than the power available in the discharge which dies down. A new discharge is established between the two electrodes and the cycle starts again.

The second phase of the life of the discharge, that of thermal and electric non-equilibrium during which up 15 to 80% of the energy is injected, is of special interest in order to stimulate a chemical reaction. The active discharges, thus created in the GlidArc-II device, can sweep almost the entire gas flow without the need for accelerating this gas flow in the vicinity of the electrodes. The displacement speed of the mobile discharge is then independent of the flow-rate and speed of the gas.

It will be possible to use the new GlidArc-II reactors for handling large volumes of gas in systems with 20 multiple stages, without the need for compressing these gases between the stages or pushing/pulling them by compressors and/or pumps cooperating with nozzles between the acceleration stages. The gases can be treated in the developed GlidArc-II structures, supplied simultaneously in a single reactor containing a certain number of concomitant and successive discharges between electrodes. These electrodes move rapidly with respect to each other, so as to stretch each discharge until the passage to its phase of thermal non-equilibrium, followed by 25 extinction and re-ignition between the nearby electrodes. Stretching of the discharges, which has become independent of the flow rate and, especially of the displacement speed of the gas (speed which can be low at the time of passage into the zone activated by the discharges), makes it possible to ensure that almost all the gas effluent is submitted to the electrons, ions, radicals and other particles excited by the discharge. This makes it possible to attain the chemical effect desired. After rapid diffusion and aerodynamic turbulence, these active 30 species, which have a relatively long lifetime, succeed in scattering even in this space which is not touched by the discharges. These phenomena contribute also to the extraordinary activity of these mobile discharges.

The following description will help to better understand the method of operation and the scope of this application. Figure 1 represents a method of execution of the device according to one embodiment. A high voltage and low intensity (a few Amperes) discharge is established between end 2 of a stationary electrode 1 and 35 a point 4' of a second electrode 3. The voltage applied between electrodes 1 and 3 is that of the secondary 6" of the transformer (voltage amplifier) 6 whose primary 6' is connected at 8 with the network. The base of discharge 4' is separated at very high speed from end 2 of electrode 1, so as to rapidly stretch the discharge and displace the mobile discharge base 4". This rapid displacement is obtained, for example, by rotating electrode 3 around axis 5. The discharge 7 is thus stretched over a great length and sweeps the peripheral zone of mobile electrode 3. When 40 the current has reached its maximum value, the power begins to decrease and the discharge enters its thermal non-

equilibrium phase. When the length of the discharge continues to grow and the sinusoidal voltage at secondary 6" of transformer 6 decreases, the discharge dies down; then it is primed again between the stationary electrode 1 and the 4' part nearest electrode 3; then the cycle begins again. As an example, we observed that, on a circular electrode 3 with 140 mm diameter rotating at a speed between 50 and 1000 rad/s, that the zone affected by the diffused discharge may extend on more than 2 rad between points 4' and 4". We have also remarked that it is not necessary that the mobile electrode be toothed, as shown in Fig. 1. In fact, small surface irregularities are sufficient for the discharge base to be "hooked" and moved with the disk at high speed. The gas to be processed no longer has to be used to drive the discharge, as it did in the case of the preceding GlidArc-I. Therefore, it is possible to fill with gas the annular space of the reactor included between the turning disk and the reactor wall and then process a certain volume of gas for a definite period of time, or introduce a desired continuous gas flow in the reactor.

Figure 2 shows the diagram of a reactor with 4 identical stages. Of course, this is only an example and it does not limit the execution of a future industrial size reactor. Each stage includes a disk d and 3 stationary electrodes offset by 120°, identified as r , s and t , each electrode being connected to a three-phase transformer phase, the disk being connected to the neutral point of the transformer. This turning disk may also be connected to the ground, which eliminates the problem of electric insulation of this moving part. The gas is introduced, for example, in k in the lower part of the reactor and extracted in l . Several gas inputs and outlets can be arranged in the same reactor. The rotating motion of the mobile electrode can be provided by an electric motor or a compressed gas motor, or even by the gas to be processed. The turning electrode may consist of a stack of identical disks d_1 through d_4 , be a conductor brush (see Fig. 3) or even be helicoidal in shape. It is understood that these representations are given only as examples and that other methods of execution may be proposed, particularly 6- or 12-phase electrical supplies. The interior part of the body of the reactor can be simply cylindrical or equipped with baffles in order to guide the gas flow, for example, vertically. Likewise, each turning electrode can be equipped with blades which can very thoroughly stir the gas to be processed. In the case of treatment of a gas loaded with solid or liquid particles or of a particularly chemically aggressive gas, it is possible to observe some wear of the fixed electrodes which, in contrast to the turning electrodes, are permanently exposed to the action of the discharge. Therefore, it may be advantageous to equip each fixed electrode with a nozzle through which to run a protective gas. Another solution consists of applying stationary electrodes with an elongated shape which allows the discharge bases to move rapidly on these electrodes. Although it is still possible, it is not necessary to resort to a cooling system for the stationary electrodes, since the intensities used are limited and, as a rule, are lower than 10 A. As an example, the power developed in a three-phase system can reach $3 \times 10 \text{ A} \times 2 \text{ kV} = 60 \text{ kW}$ per stage, which makes it possible, with a stack of 4 stages as shown in Fig. 2, to develop 240 kW on a reactor with 0.3 m diameter and 0.5 m height, so in a volume of the inner chamber of approximately 0.03 m³ for a 0.2 m turning electrode diameter.

It is possible to make good use of a stabilization inductor L per phase between the transformer and each stationary electrode. The discharge voltage U_d and the current I_d are thus out of phase with respect to the voltage at the transformer terminal U_t , as shown in Fig. 4a and 4b. Thus, the possibility exists of supplying the discharge, after the voltage at the transformer terminals has passed through its maximum and is real canceled by the energy accumulated in the inductor. Then, when the discharge dies down, full empty voltage of the transformer is available at the terminals of the electrodes.

Several gas conversion tests were performed in an experimental GlidArc-II reactor previously shown schematically on Fig. 2. Its construction, but hereby limited, is as follows: The reactor consists of four steel or nickel toothed or smooth disks, with 140 mm diameter, and twelve fixed electrodes. Said electrodes, also made of steel or nickel (shaped as curved knives) are placed symmetrically (each one offset 120°), three per stage, around disks 5 mounted on the same in fast rotation. At each stage of the reactor, each one of the three fixed electrodes is linked to one of the phases of a three-phase 8.7 kV transformer (voltage between 50 Hz phases); the disk is connected to the neutral point of the transformer. There are four identical transformers, one per disk (stage). All the mobile and fixed electrodes are placed inside a ceramic tube (possibly lined on the inside with refractory wadding), with 203 mm 10 inside diameter and 265 mm length. The tube is closed on each side by refractory plate covers. These plates accommodate the fastening and driving system of the shaft by means of a small electric motor, the refractory glass windows, the input and outlet of the gas to be treated and some probes (pressure, temperature). No part of the reactor is cooled by forced means. The reactor is leakproof and makes it possible to obtain, in its interior, pressures ranging from 0.1 to 6 bars. The electric power of the reactor is regulated by activating one, two or three fixed electrodes per stage (each injecting the 0.12 A limited current). We can also activate one, two, three or four stages of the reactor. 15 The maximum electric power of the reactor is 3 kW. However, it is quite possible to use higher power for industrial activities.

The reactor is supplied by controlled flows (by mass flow meters) of gas taken from cylinders. The reactor supply in compound initially liquid at ambient or higher temperature (for example, a heavy hydrocarbon or water) may also be provided by a dosing pump. The constant flow of said liquid, controlled by a valve and a flow-meter, can 20 thus be evaporated in an oven, to be then injected into the reactor, whether or not being previously mixed with another process fluid. The incoming fluids are mixed far from the injection spray tip, in the injection tip itself or in its vicinity. They can be preheated together or separately by means of a temperature controlled resistance oven. This last method would be preferable for an industrial reactor, in order to prevent an early O₂ + HC combustion at the time of preheating.

25 Another subject of this application consists of dividing a GlidArc-II mobile discharge reactor in some compartments. By adding (for certain tests) a more or less perforated separation, for example in the form of grillwork, we thus create a compartment of mobile electric discharges close to another compartment C, empty or partially filled with solid matter, see Fig. 2. We thermally insulate the entire reactor (for example, by using refractory felt) to save energy inside the reactor and have the temperature of the walls of two zones, that of the mobile and 30 immobile electrodes as well as that of the optional solid load, rise as high as possible. Therefore, some molecules generated in the plasma zones and penetrating the other zone can be modified in the compartment without discharges, called "post-plasma". The solid matter which may be filling the post-plasma zone may act as a contact on which we facilitate reactional exchanges between the species from the plasma zone. This matter is not necessarily known as a catalyst, but may become so in contact with the species from the plasma zone. Besides, the solid matter inserted in 35 the post-plasma zone (in most cases, we use Nickel metal chips) has a geometric surface area of a few square decimeters, which is less by a few orders of magnitude than the surface area of a traditional catalyst! The perforated partition between the zones then provides a passage for the reagents (partially consumed) and for active "long-living" species produced by the excitation of the gases by the mobile discharges. The Nickel or other electric conductor stationary and mobile electrodes can also contribute by their surface area to the plasma, in an almost catalytic post-40 treatment of the gases, vapors or liquids introduced in the reactor. In the post-plasma zone and on the surface of the

electrodes, the conversion is thus likely to be completed in the presence of said solid matter and in an environment where the temperature is naturally lower than the "temperature" in the plasma zone. The bright zone of mobile electric discharges (as well as other elements of the reactor) can be observed through windows in order to make certain of the proper operation of the reactor and to determine the temperature of the walls of the two compartments.

5 Important information may also be deduced from the plasma emission spectrum. Physics provides us with information on these atomic and molecular species, such as H⁺, OH⁺, O₂[·], CO₂[·], CO[·], H₂[·], H₃[·] (and many others) which have a sufficiently long life time to travel relatively long distances in the gas flow, even at atmospheric pressure or at higher pressure. This phenomenon is very important for the conversion of HCs known for their fragility. In fact, the action of a non-equilibrium plasma, such as the mobile discharge plasma combined with the
10 post-plasma zone, enables us to perform "gentle" transformations in this type of reactor with one or more post-plasma compartments. There, very active and metastable species (hence, having catalytic properties) make it possible to reform these HCs originating from violent reactions in the plasma zone, through deactivation on other molecules directly in the gas phase or indirectly on the surface of some electrodes or on a solid matter inserted in the post-plasma zone. It is also possible to extend the conversion of the reagents.

15 A multiple stage reactor may contain several post-plasma compartments located downstream from each or some plasma zones, so that the products of conversion by plasma may be transported there by the gas stream passing through the reactor towards its exit.

At the time of the tests, a pressure gauge shows the pressure inside the reactor; this pressure is established and controlled by a manual valve placed at the reactor exit.

20 The products leaving the reactor are first cooled in an air- heat exchanger. When they leave the exchanger, the gases and vapors are directed to a tee-piece which serves to send them either to analysis or to the exhaust chimney. We gather and weigh the liquids leaving the reactor, by condensation at 0°C. We gather also the dry gas products for chromatographic analyses. To this effect, we first send all the products to a chimney; then, when we estimate that the reactor is operating at the desired way, we send the outgoing products towards analysis. The liquids
25 deposit in a cooled flask and in an absorbent matter; then the dry gases are sucked into a syringe.

Some chemical analyses are performed, using traditional gas chromatography methods. We use three chromatographs, each intended for individual dry gases: CO, CO₂, N₂, O₂ and CH₄ for the first, hydrogen alone for the second and all hydrocarbons for the third. The water vapor stream which may exit together with some products is calculated from the material balances or quantified by cold trapping of a known volume of exiting gases.

30

EXPERIMENTAL RESULTS

Numerous feasibility tests of the natural gas (NG) reforming process were performed in the new GlidArc-II reactor. We present only the most significant tests. The composition (by % volume) of the NG originating from a commercial cylinder was: 98.7% CH₄, 0.57% C₂H₆, 0.07% C₃H₈, 0.67% C₄H₁₀ and 0.01 % C₅₊. The overall NG
35 conversion ratio is limited in almost all the tests in order to better study the individual conversion phenomena of each of the components. This conversion can obviously be much higher, for example after increase of the specific energy injected into the reagents.

Dry Conversion with Carbon Dioxide

Table 1 summarizes tests 2 through 9f on NG reforming with CO₂ alone under atmospheric pressure. The reactor was not thermally insulated (hence the high losses of energy). The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments. The temperature of the incoming gases was always equal to 22°C.

This table (as well as the following tables) is divided horizontally into three parts. The first part shows the nature and quantity of the fluids injected into the reactor, the specific energy (SE) injected into the plasma (the real electric power of GlidArc-II related to the normal hourly flow of all the incoming gases and vapors, as well as the temperature of the fluid leaving the reactor, which is equal to the temperature read inside the last plasma compartment (but not in contact with the mobile discharges). The second part of each table shows the volumes (in standard liters) of dry products of the process leaving the reactor after injection of 1 kWh of electric energy in the GlidArc-II plasma under experimental conditions. Thus, these values indicate an actual energy cost (EC) in electricity of the process at laboratory scale. This section shows also the energy cost of a unit mass of CO (other products considered "free") or of unit volume of synthesis gas (other products also considered "free") with a given H₂/CO ratio. The third part of each table shows the other results of calculations based on the experimental data: the overall rate of conversion of carbon of HC origin and possibly of CO₂ origin, the conversion rates of different hydrocarbons present in the NG, as well as the relative conversion selectivities of carbon present in the HC and possibly of CO₂ origin towards various products. The material balances were facilitated by the absence of coke, soot, tar or other pyrolytic compounds in our products (within limits not to exceed 1% expressed in mass of converted carbon).

20

Table 1

Test		2	3	4	5	6	7	9a	9b	9c	9d	9e	9f
Incoming flow	NG	10	4.7	4.7	7.4	8.9	7.9	3.9	7.5	11	15	15	15
l(n)/h	CO ₂	15	7.7	11	10	9.5	10	21	21	21	21	17	14
SE, kWh/m ³ (n)		1.7	3.4	2.2	2.3	2.3	2.2	1.6	1.4	1.2	1.2	1.3	1.5
Temp. (°C) at exit		255	255	240	250	260	265	270	250	220	220	230	210
Exit l(n)/kWh	C ₂ H ₄	1.1	0.5	1.0	1.0	1.2	1.0	0.0	0.9	1.2	1.5	1.5	1.6
	C ₂ H ₂	6.6	2.6	5.6	7.0	10	7.0	1.2	3.6	6.4	11	13	19
	CO	225	170	197	196	178	226	191	249	253	237	233	184
	H ₂	157	98	165	159	182	149	36	97	140	172	208	246
H ₂ /CO, mol/mol		0.70	0.58	0.84	0.81	1.02	0.66	0.19	0.39	0.55	0.72	1.12	1.34
SE CO, kWh/kg		3.5	4.7	4.1	4.1	4.5	3.5	4.2	2.9	2.5	2.4	2.3	2.3
EC SG, kWh/m ³ (n)		2.6	3.7	2.8	2.8	2.8	2.7	4.4	2.9	2.5	2.4	2.3	2.3
C (%) conversion in	NG	48	70	56	56	52	58	61	50	41	36	37	40
	CO ₂	37	53	39	44	41	49	25	31	29	26	26	28
HC conversion (%)	CH ₄	48	70	56	55	52	58	62	50	41	36	37	40
	C ₂ H ₆	47	64	46	53	50	50		35	30	30	34	39
	C ₃ H ₈	65	82	65	66	62	68	64	57	48	45	46	50
	C ₄ H ₁₀	47	68	53	65	61	63	63	57	23	38	40	47
C (%) conversion selectivity towards	C ₂ H ₄	0.9	0.6	0.9	0.9	1.2	0.8	0.1	0.7	0.9	1.1	1.3	1.4
	C ₂ H ₂	6.6	2.9	5.3	6.5	10	5.8	1.0	2.8	4.8	8.2	11	16
	CO	93	96	94	92	89	93	99	96	94	90	87	82

Comparison of our present results of NG conversion with CO₂ with our old results obtained in a GlidArc-I (see Table 2 of BF 2758317) confirms the superiority of the new GlidArc-II device. This comparison is illustrated in

25 Table 1a.

Table 1a

Test	SE kWh/m ³ (n)	CO ₂ /NG mol/mol	Preheating °C	EC CO kWh/kg	EC SG kWh/m ³ (n)	Conv. NG	Conv. CO ₂	H ₂ /CO mol/mol
Old G12	1.4	1.3	165	5.3	3.6	11 %	12 %	0.82
New 9d	1.2	1.4	22	2.4	2.4	36 %	26 %	0.71

The energy costs for the production of 1 kg of CO or 1 m³(n) of SG are thus respectively 2.2 or 1.5 higher using GlidArc-I with respect to the new test in GlidArc-II, with incoming cold gas and the more advantageous SE.

5 Best performances are also observed now regarding the quantities of exiting acetylene.

We emphasize also that we performed "dry" reforming of ethane, propane and butanes present in the NG (used as reagent). After precise balances and analyses (see Table 1), we determined that the conversion of these HC heavier than methane is more advanced, despite very high excess of methane in the studied NG. This indicates again that the reforming process with CO₂ of hydrocarbons heavier than methane would be easier.

10 The dry reforming process assisted by mobile discharges can then be applied, regardless of which natural gas (or other mixture of hydrocarbons) is to be converted. For example, we are thinking of the different biogases or certain gas resources like mixtures of hydrocarbons and carbon dioxide. These gases can thus be upgraded without costly extraction of CO₂. Moreover, when a "clean" energy source (solar, hydraulic, nuclear, etc.) or "free" energy source (exhaust gas from thermal engines, etc.) is available, we will be able thus to recycle the carbon dioxide, now a major problem.

Steam Reforming

Table 2 summarizes tests 31 through 34 of natural gas steam reforming. This time, the NG carried by the steam, enters preheated at a higher temperature than before. The conversion took place under atmospheric pressure. The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments.

20

Table 2

Test		31	32	33	34
Incoming flow l(n)/h	NG	3.9	7.5	11	15
	H ₂ O	9.7	10	10	11
SE, kWh/m ³ (n)		3.1	2.4	2.1	1.7
Temperature, °C	entry	165	150	140	140
	exit	305	305	290	270
Exit l(n)/kWh	C ₂ H ₄	0.6	1.4	2.2	2.6
	C ₂ H ₂	1.7	6.7	13	22
	CO	53	78	86	83
	H ₂	193	275	325	326
H ₂ /CO, mol/mol		3.65	3.52	3.80	3.90
EC CO, kWh/kg		15	10	9.4	9.6
EC SG, kWh/m ³ (n)		4.1	2.8	2.4	2.4
C Conversion (%)		63	53	46	41
HC conversion (%)	CH ₄	31	52	44	39
	C ₂ H ₆	62	56	51	47
	C ₃ H ₈	98	98	97	97
	C ₄ H ₁₀	72	67	65	50
Conversion selectivity of C (%) towards	C ₂ H ₄	2.1	2.8	3.7	3.7
	C ₂ H ₂	5.6	14	22	32
	CO	88	79	70	59
	CO ₂	4.6	4.0	4.0	5.5

Comparison of our present results of NG steam reforming with our old results obtained from experiments conducted in the GlidArc-I reactor (see BF 2758317) confirms also the definite superiority of the new GlidArc-II device described hereinabove. Table 2a illustrates these differences and recalls the conditions of the comparative tests.

5

Table 2a

Test	SE kWh/m ³ (n)	H ₂ O/NG mol/mol	Reaction temperature	EC CO kWh/kg	EC SG kWh/m ³ (n)	Conv. NG	H ₂ /CO mol/mol
Old G5	1.2	1.1	680°C	13	3.0	24 %	4.5
New 34	1.7	0.73	270°C	9.6	2.4	41 %	3.9

10 We now obtain much more acetylene: 22 l(n)/kWh instead of 9.6 l(n)/kWh before. We will point out that the temperature of the reaction (or, rather, that of the interior of the GlidArc-II reactor) is much lower! Therefore, it appears that the hydrocarbon load placed into closer and more prolonged contact with the zone of mobile discharges dispersing the energy along the passage of the reagents is much more efficient than the gliding arcs of GlidArc-I injecting only a portion of the energy into the gas. We emphasize also that we perform steam reforming of ethane,
 15 propane and butanes present in the natural gas. On the basis of our chemical analyses and our balances of material entering and leaving the GlidArc-II reactor, we determine that the conversions of HCs heavier than methane are much more distinct than that of methane. This indicates to us that, thanks to this steam reforming process of hydrocarbon feeds containing increasingly heavy hydrocarbons, their conversion is achieved increasingly more easily, and this with the same specific energy applied to the entering feed. The steam reforming process assisted by
 20 mobile discharges may then be applied to any natural gas (or other mixture of hydrocarbons) to be converted.

Mixed Steam and Carbon Dioxide Reforming

25 Table 3 summarizes tests 11 through 15 of NG reforming with an H₂O/CO₂ mixture. The three reagents are injected at 22°C and then H₂O is in fog form. The conversion takes place under atmospheric pressure. The reactor was not thermally insulated, hence the high energy losses. The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments.

Table 3

Test		11	12	13	14	15
Incoming flow l(n)/h	NG	9.4	9.4	9.4	8.4	8.4
	CO ₂	10	10	10	7.7	7.7
	H ₂ O	2.5	2.8	4.9	4.9	8.7
SE, kWh/m ³ (n)		1.6	1.7	1.6	1.8	1.6
Temp. (°C) at exit		290	230	240	250	230
Exit l(n)/kWh	C ₂ H ₄	1.3	1.2	1.1	1.3	1.2
	C ₂ H ₂	9.1	8.8	6.4	9.4	8.0
	CO	195	193	207	178	161
	H ₂	176	188	171	229	196
H ₂ /CO, mol/mol		0.90	0.98	0.82	1.29	1.22
EC CO, kWh/kg		4.1	4.1	3.9	4.5	5.0
EC SG, kWh/m ³ (n)		2.7	2.6	2.6	2.4	2.8
% conversion of C to	NG	46	48	57	53	50
	CO ₂	28	35	32	40	39
% conversion of HC	CH ₄	42	48	56	54	50
	C ₂ H ₆	37	40	52	52	42
	C ₃ H ₈	63	59	66	64	57
	C ₄ H ₁₀	83	56	69	48	58
Conversion selectivity of C (%) towards	C ₂ H ₄	1.2	1.2	1.0	1.3	1.4
	C ₂ H ₂	8.4	8.3	5.8	9.4	8.9
	CO	90	90	93	89	90

We previously demonstrated the feasibility of a HC conversion process (without the use of traditional catalysts) assisted by gliding arcs plasma (GlidArc-I) in simultaneous presence of carbon dioxide and steam (BF 2758317). The comparison of our present results from this mixed NG reforming with our previous results indicates also the definite superiority of the new GlidArc-II device. Table 3a illustrates these differences and recalls some comparative test conditions.

Table 3a

Test	SE kWh/m ³ (n)	H ₂ O/CO ₂ / NG	Reaction Temp.	EC CO kWh/kg	EC SG kWh/m ³ (n)	Conv. NG	Conv. CO ₂
Old G23	1.3	0.4/0.3/1	675°C	9.1	3.3	16 %	3.2 %
New 13	1.6	0.5/1/1	240°C	3.9	2.6	57 %	32 %

Again we note a broad range of ratios of two oxidizers which can be used. Although our examples are given for H₂O/CO₂ values between 0.25 and 1.1, the fact of being able to use only one oxidizer (see Table 1 and Table 2) enables us to expand this ratio for values between 0 and infinity. Thus, all the H₂O/CO₂/NG feeds can be converted in GlidArc-II reactors without prior separation of the components.

We note the absence of soot, cokes or other products which would be undesirable at the time of the conversion of heavy hydrocarbons, such as the butanes present in considerable quantity in the NG. On the other hand, the increasing fragility of increasingly heavy HCs is a "plus" for our process from the point of view of energy cost for the production of CO as well as for other valuable unsaturated products. This is a strong point of our process with respect to traditional processes which are confronted with problems of deposition of cokes and tars, especially in the presence of hydrocarbons heavier than methane.

Lastly we point out the considerable quantities (but at adjustable ratio) of unsaturated HCs in our products from conversion assisted by GlidArc-II plasma. They are of additional value as final commercial product (acetylene) or as raw material for other organic syntheses.

Mixed Steam and Oxygen Reforming

5 Table 4 summarizes tests 41 through 47 on NG reforming simultaneously with an H₂O/O₂ mixture. The question was: is it possible to steam reform a NG with a small amount of oxygen to improve the energy cost and to approach the H₂/CO ratio of 2? The three reagents are injected through the same nozzle at temperature over 100°C (except for test 45), in order to evaporate water. The conversion takes place under atmospheric pressure. The reactor is not thermally insulated; hence, the high losses of energy. The stationary and mobile electrodes are made of
10 stainless steel: no post-plasma compartments.

The results of this set of tests show that it is possible to oxidize the hydrocarbon feed in deficit, the O₂/HC molar ratio being between 0.06 and 0.38. Another positive point which could lead to choose the use of steam beside the oxygen is that it is possible to create a relatively large quantity of ethylene and acetylene in the SG (see tests 41, 15 42 and 44). Comparing tests 31 and 45, 32 and 44 or 33 and 43, we see that a limited addition of H₂O makes it possible to lower the EC; we thus demonstrate that it is possible to add a well proportioned quantity of oxygen to achieve a particular objective. We note that the overall rate of NG conversion (at this time limited in our tests) can be brought to 100% by increasing the power of the reactor and/or reducing the NG flow entering the reactor (this again increases the SE). We add also that, by analyzing individually the conversion rates of each HC, we determine that the heavier HCs react more easily. Our partial oxidation and steam reforming process assisted by mobile discharges
20 could thus be applied, regardless of the HC content of a NG (or other mixture of hydrocarbons) to be converted.

Table 4

Test		41	42	43	44	45	46	47
Entering flow l(n)/h	NG	15	15	7.5	11	7.5	6.1	4.7
	O ₂	0.86	1.7	1.8	1.8	1.8	1.8	1.8
	H ₂ O	9.2	9.3	9.3	4.3	4.3	2.6	2.6
SE, kWh/m ³ (n)		1.8	1.6	2.5	2.4	2.9	3.8	4.4
Temperature in °C	Entry	134	162	187	175	72	194	200
	Exit	330	320	310	310	300	280	300
Exit l(n)/kWh	C ₂ H ₄	2.7	3.3	1.5	3.4	2.1	1.7	1.0
	C ₂ H ₂	13	13	2.8	12	5.2	3.8	1.5
	CO	90	103	79	102	95	88	77
	H ₂	297	322	213	286	255	213	174
H ₂ /CO, mol/mol		3.28	3.11	2.71	2.79	2.69	2.43	2.27
EC CO, kWh/kg		8.8	7.7	10	7.8	8.4	9.1	10
EC SG, kWh/m ³ (n)		2.6	2.3	3.4	2.6	2.9	3.3	4.0
% C conversion into NG		38	40	57	51	59	66	73
% O ₂ conversion		51	57	76	45	83	89	89
% HC conversion	CH ₄	37	38	56	50	58	65	72
	C ₂ H ₆	18	28	35	13	33	37	44
	C ₃ H ₈	96	96	97	97	97	98	98
	C ₄ H ₁₀	45	64	83	67	84	92	95
C (%) conversion selectivity towards	C ₂ H ₄	3.7	4.1	2.7	4.5	3.3	2.8	1.9
	C ₂ H ₂	19	18	5.8	18	8.9	7.4	3.4
	CO	69	72	81	73	82	84	86
	CO ₂	7.5	5.0	10	4.4	5.6	5.4	8.3

At the time of a short series of preliminary limited power tests, we replaced all the electrodes of GlidArc-II (made of stainless steel) with those made of Nickel metal. Without changing the body of the reactor, we replaced also two sections of the reactor with two inserts (with 19 cm diameter and 5 cm thickness) containing Ni chips (disconnected from the power supply). Thus, the gas first came in contact with the mobile discharges between the Ni electrodes (first stage), then it passed through the chip zone to take again the second discharge zone followed by a second Ni chip zone. The internal walls of the reactor were lined with a double layer of refractory felt in order to reduce the thermal losses of the device and to operate at the highest possible temperature. Other inert bodies, such as large fragments of ceramic brick or copper chips could also be placed instead of Ni chips for some comparative tests.

The presence of apparently inert matter in the post-discharge section considerably modified the nature and quantity of the products from the conversion. Acting on the nature of the solid matter placed in contact with a gas flow originating from electric treatment in the plasma zone of mobile electric discharges, we can obtain more or less unsaturated hydrocarbons, almost block the production of hydrogen and acetylene on large fragments of copper metal, regulate the H₂/CO ratio, etc. This is a very strong effect of the matter inserted in the post-plasma zone on the chemical composition of the products!

15

Partial Oxidation in Air, in Oxygen-Enriched Air or in Pure Oxygen

Table 5 summarizes 51 through 59 NG reforming tests in a NG/N₂/O₂ system, without any water vapor added. Whenever we used the term "added" we emphasize the external provenance of this reagent which may appear in any case (but in a very small quantity) as product of the (5), (7) and/or (8) reactions. The partial oxidation of a NG with oxygen-enriched air (for example, of membrane provenance) is much less expensive and less dangerous than oxidation with pure oxygen of cryogenic origin. The reagents are injected through the same nozzle at 28°C. The conversion takes place under atmospheric pressure. The reactor is thermally insulated by refractory wadding to reduce the large losses of energy (except for test 51). The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments.

Table 5

Test		51	52	53	54	55	56	57	58	59
Incoming flow l(n)/h	NG	4.6	15	15	15	12	15	15	15	15
	O ₂	1.8	4.6	6.0	7.4	7.4	8.6	10	12	14
	N ₂	0.0	17	22	28	28	21	20	18	14
O ₂ /NG, mol/mol		0.38	0.31	0.40	0.50	0.62	0.58	0.69	0.78	0.97
SE, kWh/m ³ (n)		5.6	0.97	0.83	0.50	0.71	0.78	0.76	0.77	0.76
Temperature (°C)	exit	285	460	490	510	500	590	640	650	830
Exit l(n)/kWh	C ₂ H ₄	2.0	2.9	2.6	4.3	3.4	4.6	5.3	1.0	4.2
	C ₂ H ₂	4.9	4.3	4.1	2.8	1.7	1.7	1.5	1.0	4.2
	CO	81	159	177	206	187	241	261	241	265
	H ₂	163	334	336	320	276	314	318	289	307
H ₂ /CO, mol/mol		2.02	2.10	1.90	1.55	1.47	1.30	1.21	1.20	1.16
EC CO, kWh/kg		9.9	5.0	4.5	3.9	4.3	3.3	3.1	3.3	3.0
EC SG, kWh/m ³ (n)		4.1	2.0	1.9	1.9	2.2	1.8	1.7	1.9	1.7
% Conversion of C to % Conversion of O ₂	NG	71	49	55	57	63	65	63	76	88
		95	82	87	87	91	95	95	97	98
% HC conversion	CH ₄	71	48	53	56	62	64	62	76	89
	C ₂ H ₆	32	-23	-8.5	5.2	19	28	29	57	87
	C ₃ H ₈	90	95	97	97	98	99	99	99	100
	C ₄ H ₁₀	94	96	95	99	99	100	100	100	100
C(%) conversion selectivity towards	C ₂ H ₄	3.6	3.8	3.4	3.2	2.6	3.9	2.8	2.2	1.9
	C ₂ H ₂	9.9	7.8	3.7	2.3	1.5	1.4	0.8	0.6	1.8
	CO	82	79	81	84	82	76	74	73	65
	CO ₂	4.6	8.0	11	10	14	21	22	25	32

All the results of this series of tests show us that it is preferable to convert a NG when the interior of the reactor attains the highest possible temperature. Despite the presence of a large nitrogen ballast (between 46 and 59% vol. in the entering flow), we can maintain, thanks to the energy and the active species present in the plasma, a reactional environment favoring the evolution of the HC partial oxidation reactions. This is seen at the level of very high temperatures in the reactor. This series of tests shows then the feasibility of partial oxidation of the HCs also with atmospheric air. This oxidation can also be carried out with very high oxygen deficit, but it is possible only in the presence of mobile electric discharges; otherwise, the purely auto-thermal process stops very soon (the chemical inertia of the reactor is very small).

A large ballast (up to 40% by volume) of CO₂ present in some NGs which we have also simulated and tested, does not prevent a proper development of the conversion of these NGs into SG. This ballast can be comparable to the inert nitrogen ballast, although a fraction of CO₂ may participate actively, via reactions (4), (4a) and (5), in the production of CO, which increases the content of valuable product.

For a pressure higher than 2 bars (test 58a) and other parameters significantly near those of test 58, we observe all the slightly improved performances (from 10 to 30%). However, when the pressure is again increased to 6 bars at the time of preliminary tests, we observe an increasing amount of soot, especially for O₂/NG ratios < 0.5.

The results of this series of tests teach us that it is preferable to convert a NG when the O₂/NG ratio reaches a value slightly exceeding 0.5. At this level, we obtain very good results with total conversion of carbon and oxygen, particularly under pressures over 1 bar and when the interior walls of the reactor attain a temperature near 1100°C. Under these conditions, we can also approach a desired H₂/CO ratio of 2.

Now we consider the limit of 6 bars as the maximum with which our device operates in stable fashion. Besides, we aim at developing partial oxidation of HC under relatively low pressures for specific applications,

such as chemical conversion of gas associated with oil (otherwise burned in flares at almost atmospheric pressure), of biogases produced in low pressure digesters, of hydrocarbon permeates originating from membrane separation, etc. Our process at relatively low pressure thus makes it possible to avoid high energy consumption compressors and facilities at high degree of technicity connected with the traditional high pressure technology of the catalytic auto-thermal process.

Comparison of our present results with the results obtained from the literature indicates the superiority of the new GlidArc-II device (described hereinabove) with respect to a traditional O₂/HC burner used in an auto-thermal process. For reference, we take the details published by the Haldor Topsoe company (Denmark) in the article by CHRISTENSEN and PRIMDAHL previously mentioned. Although the information is not complete, we can establish some balances of material of the industrial process using only the chemical energy of more or less exothermic reactions (6) through (8). Without any information on the NG treated, we consider it comparable to pure methane. Table 5a summarizes the data (marked HT) taken from this article.

Another comparison is made with respect to very complete data published in November 1995 by S.C. NIRULA in "Synthesis Gas, Report No. 148A", SRJ International, Menlo Park, California. NIRULA's report provides some information on the volume of the industrial reactor (94 m³), the flow rate of entering gases (200,000 m³(n)/h) and outlet temperature (1350°C). The data and balances (recalculated by us) are also inserted in Table 5a under a SRI reference.

Table 5a

Ref.	Pres. (bars)	O ₂ /C	H ₂ O/C	Preheating (°C)		H ₂ /CO	SG/NG	Sel. (%)	
				NG/H ₂ O	O ₂ /H ₂ O			CO	CO ₂
HT-1	34	0,55	2,5	660	560	3,63	2,70	60	40
HT-2	35	0,60	3,0	605	505	4,02	2,70	55	45
HT-4	25	0,58	1,9	525	230	3,29	2,59	61	39
HT-5	25	0,54	1,4	525	230	2,84	2,61	70	30
SRI	68	0,66	0,51	371/295	149	2,10	2,66	83	17

First of all, we note that these are thermo-catalytic processes under high pressure. The HCs, confronted with a relatively oxygen-rich flame (theoretically, one should stop at O₂/HC ~ 0.5) at over 2000°C, are consumed preferentially towards CO₂ and H₂O, according to reaction (8) rather than (7), leaving large quantities of unconsumed HCs (especially methane, the chemically sturdiest). It is only in the presence of a large mass of a fragile catalyst that the conversion of the HCs is completed according to the endothermic reforming reactions (1) or (1a) and (4) or (4a) on a catalytic bed exposed to very high temperatures (1100-1400°C). This catalyst and its support should then present very high resistance and very good stability under severe conditions.

In no industrial example or pilot test do CHRISTENSEN and PRIMDAHL mention the O₂/C ratio lower than 0.54 and the H₂O/C ratio lower than 0.58. Instead, on the contrary, they emphasize the need for adding at least these quantities of oxygen and water vapor in order to ensure proper operation of their burner, requiring also special recirculation. We, instead, can reduce these ratios respectively to 0.06 and zero (tests without water vapor), since we have another adjustment button: the very active energy of mobile electric discharges added to the very sub-stoichiometric flame!

Therefore, we demonstrate, for the first time, the feasibility of a new NG conversion assisted by mobile discharge plasma in the presence of oxygen or of oxygen-enriched air, or of atmospheric air with possible addition of steam. This process is illustrated in Tables 4 and 5 through the conversion of a model NG in a new GlidArc-II reactor in which the plasma zone (with all the electrodes) is brought to a temperature not over 1150°C. Another post-plasma zone communicates directly with that of the plasma. This post-plasma zone, at a temperature lower than 1100°C can be partially filled with a solid metal or ceramic matter which, in contact with a flow of products of treatment of the hydrocarbon feed with plasma, becomes active and participates in a total or almost total conversion of the HCs into SG with more or less co-generated ethylene and acetylene. In the presence of oxygen and, possibly, of the steam added, we can thus convert all the HCs, such as CH₄, C₂H₆, C₃H₈ and C₄H₁₀ into synthesis gas and also, partially, into valuable products: C₂H₄ and C₂H₂, without using traditional catalysts.

A broad range of ratios of the two oxidizers (O₂ and H₂O) with respect to the NGs may be used. Our examples are given for O₂/NG values between 0.06 and 0.97 and H₂O/HC between 0 and 2.5, but it is evident that we can further expand at will these two terminals from zero to infinity, since our mobile discharges can be generated in pure water vapor as well as in pure oxygen. Thus, all the H₂O/O₂/NG mixtures can be converted in the reactor described herein. According to need, we can in this manner obtain synthesis gas with an H₂/CO ratio near 2 for the FT synthesis of synthetic oil, or of methanol, or a highly hydrogen-rich synthesis gas for the synthesis of ammonia, or yet a gas highly rich in CO for Syntheses called "oxo" ..., without being limited to these examples. As previously, we note the total or almost total absence of soot, coke or other undesirable products at the time of the NG conversion.

We point out also the presence of considerable (but adjustable in content) quantities of unsaturated hydrocarbons C₂H₄ and C₂H₂ in our conversion products. These are of additional value, since, mixed with the synthesis gas, they facilitate construction of hydrocarbon chains at the time of the FT synthesis. Thus, formed at the same time as CO and H₂ during the conversion of hydrocarbons in mobile discharges, these unsaturated molecules will contribute to the direct application of an improved FT synthesis of liquid hydrocarbons.

In most of the tests involving O₂ or CO₂, we determine a conversion of the initial ethane which is considerably less than that of methane, propane and butanes. In some tests, we even have more ethane leaving than entering, hence a negative conversion or rather a synthesis of ethane. This effect, apparently strange, nevertheless confirms the feasibility of the methane dimerization reaction (7) by a radical process involving probably two CH₃ fragments formed after gentle oxidation by the oxygen (excited?) originating from O₂, introduced as plasma-forming gas or by a radical deriving from plasmatic dissociation of CO₂. This production of ethane starting from methane is very visible in the presence of certain bodies inserted in the post-plasma zone.

Production of Hydrogen, Acetylene and Ethylene Starting from Hydrocarbons

The partial pyrolysis of methane yields a considerable quantity of Hydrogen at largely lower price than that of water electrolysis, since the previously mentioned reaction (2a) shows a standard enthalpy (at 1 atm and 298 K) of 125.5 kJ/mol H₂, while, for the electrolysis, this enthalpy is 285.8 kJ/mol H₂. In the case of Pyrolysis, at the same time other highly valuable products are recovered, such as acetylene and, in smaller amount, ethylene, in accordance with reaction (2).

However, the pyrolysis of methane carried out in the thermal plasmas of arcs or of traditional plasma torches causes almost total destruction of the methane, in accordance with reaction (2b) expected for complete thermodynamic equilibrium. Our thermodynamic calculations for 1.4 atm, applied to partial equilibrium (barring

the appearance of graphite) nevertheless indicate the possibility of running the reactional path (2a). For that, the required conditions are as follows: raising the temperature to approximately 1700 - 2300 K and quickly quench the system, bringing it down to temperatures around 700 K in order to protect the fragile acetylene (or ethylene) molecule. Thus, the production of soot via reaction (2b) is prevented.

5 Table 6 presents confirmation of these assumptions. Our tests under atmospheric pressure and at limited power are very encouraging. The same NG, diluted by hydrogen (in order to prevent coking) is introduced, under control, into the GlidArc-II reactor. The reactor is not thermally insulated and the gases enter at ambient temperature, hence the large losses of energy. The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments.

10 The material balance still indicates the presence of soot which we must find in the products. In fact, in a filter at the outlet of the reactor, we collect a small amount of very fine, dry soot, with nanometric granulation and high resistance to thermal graphitization which appears only at the end of very long heating at 2800 °C.

Table 6

Test		81	82	83	84
Incoming flow	NG	1.2	1.2	3.8	7.0
I(n)/h	H ₂	20	10	20	20
H ₂ /NG, mol/mol		17	8.2	5.2	2.9
SE, kWh/m ³ (n)		1.5	2.9	1.5	1.2
Temperature (°C)	exit	235	260	290	340
Exit	C ₂ H ₄	1.5	1.4	1.7	3.0
I(n)/kWh	C ₂ H ₂	5.3	6.3	17	24
	H ₂	23	37	75	112
% Conv. of C from	NG	41	60	44	34
	CH ₄	41	60	43	34
% Conversion	C ₂ H ₆	36	19	37	41
of HC (%)	C ₃ H ₈	51	71	61	52
	C ₄ H ₁₀	74	84	65	42
C (%)	C ₂ H ₄	19	12	11	8.4
conversion	C ₂ H ₂	66	54	68	66
selectivity towards	soot	13	33	20	25

15 The selectivities of NG pyrolysis towards acetylene, ethylene and soot indicate that reaction (2b) of the complete pyrolysis is in the minority. This is surprising at this low level (~ 300°C) of average temperatures of the outgoing gases. In fact, the methane entering the active discharge is treated at certainly much higher "temperature" (since this concept is reserved for the complete thermodynamic equilibrium), but the products of this plasma

20 pyrolysis are soon abandoned at relatively low temperature, since the mobile discharge is no longer present.

Our tests reopen a very important technology method (forgotten, however, since it involves acetylene produced from calcium carbide). In fact, acetylene was a good base for the syntheses of various final or intermediate products. Moreover, the extraordinary quality of the other product, soot, leads us to believe in a future renewal of the method mentioned.

25

Upgrading Conversion of Heavy Hydrocarbons

Fuel production discards a "bottom of the barrel" consisting of a very heavy residue. This black and viscous residue, resulting from the extraction of light products from the crude, is a very hydrogen-poor hydrocarbon. In order

to convert it into gasoline or other valuable liquid products, it would be necessary to restore the equilibrium of its molecular deficit either by adding hydrogen or by removing carbon, both operations being difficult and very expensive due to the excessive content of metals, sulfur and nitrogen. These elements, present in the crude in relatively small quantity, have ended by concentration (despite subsequent purifications) in this last product of the all 5 refining operations.

Facing the scarce external outlets for heavy fuels, but also the increasing ratio of heavy oils in proven reserves, the Refiner must then in the end increasingly resort to so-called conversion units. This conversion of refinery residues (or, possibly, of very heavy primary feeds) into gasoline or diesel oil, although very expensive, has regained the interest of the oil companies. It would also offer commercial compensations: deeper conversion of 10 residues in gasoline and other valuable liquids. The most effective technological solution is to be chosen. Liquid HC (naphtha, diesel oil) being by far the most desirable, this is the reason why the processing techniques which lead to obtaining maximum yields of these products are preferred by Refiners.

The sulfur and metal contents in the residues may attain very high values, making it much more difficult to treat and upgrade the products. The metals (V, Na) are undesirable poisons for the traditional hydro-treatment 15 catalysts and render the hydrogen processes inoperative.

In the "bottom of the barrel", we find a C/H ~ 1 atomic ratio. In order to upgrade this residue, several methods are possible, depending on the agents which are going to allow attack of the molecules and/or segregation in cuts:

- The most brutal agent seems naturally to be oxygen: partial oxidation may lead to total destruction 20 of the carbon skeletons; gasification is almost complete, although with the formation of fatty soots for which it is necessary to find an upgrading method. Nevertheless, we prefer "gentle" plasma oxidation leading to a large portion of liquid fraction lighter than the processed feed.
- In order to improve the C/H ratio of the residue, obviously, hydrogen can be added. However, in addition to the high cost, this requires highly pure hydrogen, without CO, which is poison for the 25 catalysts. Moreover, it is almost impossible to hydrogenate and to hydrocrack directly a heavy residue, due to the presence of high concentrations of metals, sulfur and nitrogen compounds poisoning the catalyst.
- It is also possible to imagine attacking the heavy load with these two reagents at the same time, i.e. by water at high temperature. Steam-gasification is then obtained, leading to the production of gas 30 highly rich in hydrogen. Nevertheless, we advocate a "gentle" steam-gasification assisted by electric discharge plasma, leading to a large portion of liquid fraction lighter than the processed feed.
- Lastly, we will mention steam cracking of heavy feeds at very high temperature for the production of a gaseous phase containing hydrogen, acetylene, ethylene, olefins and aromatic di-olefins. But 35 we prefer to recover also liquids via our process assisted by electric discharges...

Several preliminary tests were performed in the reactor in vertical position by introducing fogs of heavy HCs. These fogs originated from preheating (up to 370°C) of liquid hydrocarbons (such as gasoil or n-C₁₆) driven with a process gas (dosed by flow meter) by means of a dosing pump through a tubular oven heated by electric resistance. The liquid would evaporate partially in the oven, thus forming a mixture of gas/vapors/droplets which 40 entered through the upper part of the reactor to undergo four stages of the mobile discharge. Part of the liquid would

be thrown on the inner walls of the reactor by centrifugal force from rotation of the central disks driving the rotation of the gas (and of the fog) filling the reactor. A liquid film thus would flow slowly on the walls while being in contact with the post-discharge gas containing multiple active radicals. The products of the conversion exited through the lower part of the reactor where they were separated in a trap at 0°C into liquids and gas/vapors for qualitative and 5 quantitative analysis. For the liquids, we use gas chromatography (a FID detector and a column capable of properly separating the hydrocarbons from C₅ to C₂₀).

Tests with pure n-C₁₆ (Hexadecane or otherwise Cetane) simulating a heavy feed were performed in the presence of various plasma-forming gases: H₂ and/or N₂, N₂/H₂O, N₂/O₂, CH₄/N₂/O₂ or CO₂/N₂/O₂ in different proportions. The presence of oxygen seemed puzzling, but we envisioned a process in which part of the heavy 10 hydrocarbons (considered a waste to be upgraded) would be converted in place into Hydrogen used to hydrogenate the other part of the load. Therefore, it was not a total gasification of heavy hydrocarbons that was sought, but, rather, a conversion to less heavy HCs. We applied different pressures (between 1 and 3 bars), different proportions of gases in the mixtures, high input temperature, etc. Thus, the n-C₁₆ flow rate would vary between 0.16 and 0.50 kg/h, the flow rate of the incoming plasma-forming gas between 1.4 and 2.4 m³(n)/h, the electric power of the reactor between 15 0.7 and 2.0 kW. The most important variable of this set was found to be the plasma-forming gas. It should be noted that, regardless of which plasma-forming gas, the same type of "useful" light product is always observed in the liquid recovered: the alpha-olefins centered on C₁₁ (between C₆ and C₁₅).

- Six tests were performed with Hydrogen. We thus demonstrated that GlidArc-II can operate with this gas at pressure up to 3 bars. The quantity of the "light" liquid fraction in the liquid product existing was less than 5%. At the same time, we observed very pronounced gasification up to 50% (mainly towards acetylene and ethylene). The increase of the input temperature of the feed and of the gas (for almost equal specific energies and pressures) would seem to play a positive role from the point of view of the main objective.
- One test was performed for 2 bars with Nitrogen. We first demonstrated that GlidArc-II can operate with this gas at high pressure (3 bars) and that this Nitrogen plasma yields less fraction C₆-₁₅, less HC gas (especially CH₄) and more soot in the gas (grayish smoke) and in the reactor (deposit).
- Seven previous tests were performed with H₂ + N₂ mixtures for pressures between 2 and 3 bars. However, the most important variable was the concentration of Hydrogen (from 100% to 0%). For similar conditions, it is possible to see that the increase in H₂ content causes the overall yield of the C₆-₁₅ liquid product to rise and that the increase of the injection temperature of the feed for a low H₂ content does not yield the result desired (the result is better at a lower temperature with the availability of a 90% H₂ plasma-forming gas). The quantity of the liquid fraction concerning C₆-₁₅ in the liquid product exiting was always less than 5%. We observed less pronounced gasification of the feed when the H₂ content is reduced. It would appear that transfer of N₂ excitation towards H₂ or NH radicals plays a positive role. The role of the hydrogen plasma at low temperature seems to be limited, perhaps when an additional medium intervenes in the system. This analysis seems to be reinforced by our experiments conducted as a function of the gas volume and of the nature of the gas in which the role of the hydrogen plasma alone in the conversion phenomenon seems to remain relatively low.

The first conclusions which we draw from this are that the hydrogen plasma (at low temperature) hardly acts on liquid HCs (fine droplets) and that the experimented reduction conditions do not appear to be very favorable towards obtaining major conversion of heavy HCs into light liquid fractions. We note a high presence of acetylene and of alpha-olefins. It is, therefore, imperative to explore other plasma-forming gases as follows:

- 5 • A test with an N₂ + H₂O mixture (very moist Nitrogen) was performed for 2 bars. We demonstrate first that GlidArc-II can operate with this mixture, which possibly opens a new approach for partial steam cracking of heavy HCs at relatively low temperature and at low pressure. The test yields better conversion into useful liquids (6% instead of 1.3% in dry Nitrogen).
- 10 • Let us say immediately that a presence of Oxygen pertains only to the initial gases entering the reactor; in the plasma zone, a controlled oxidation occurs, which definitely produces: H₂, CO, CO₂ and H₂O as final products of the radical reactions in which H, OH, CH₃, CH₂, CH and other radicals intervene. Such reactions, in the presence of small amounts of oxygen, can be performed on a large scale only in the presence of a catalyst in homogeneous phase: the GlidArc-II plasma. Therefore, this would be an incomplete and "gentle" combustion which stops in a cracking phase of the heavy HCs, in the presence of a hydrogenating (H₂) or functionalizing agent (OH or CO, knowing that alcohols and ketones could be considered as fuels). Sixteen tests were performed for plasma-forming gases (impoverished air) containing 3.3 to 15% O₂ (thus still in the presence of Nitrogen) and CH₄ or CO₂. Another test with CO₂ is included in this series, since it is known that this gas is easily decomposed in a plasma into CO and very active Oxygen *in statu nascendi*. The pressures vary from 1.6 to 2.3 bars. We demonstrate that GlidArc-II can also function as an electro-activator of a partial oxidation, in absolute safety (not the least accident during all the experimentation)! At the same time, we observe very pronounced gasification of the load into CO and CO₂, as well as into HC gas - but this is a price to pay to prevent consumption of the Hydrogen originating externally. This conversion into CO and CO₂ supplies heat which, in principle, will cause low consumption of electric energy in a process in which GlidArc-II will serve only to maintain this cracking oxidation.
- 15
- 20
- 25

In conclusion, the experiments conducted in the same conditions of pressure and temperature, although with plasma-forming gases consisting of different CH₄ + air, CO₂ + air or N₂ + O₂ mixtures, all yielded better results than the experiments in "Hydrogen" medium. We observed very few aromatic compounds in the liquid products and practically no CH₄ in the gaseous products (basically ethylene and acetylene for the HCs). By this method, we obtain in the liquid products up to 54% compounds between C₆ and C₁₅ with very pronounced maxima near C₁₀ - C₁₁.

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CO + H₂O ⇌ CO₂ + H₂ (Simple and Inverse) Shift

Table 7 shows the feasibility of these two reactions in the GlidArc-II reactor without the presence of a catalyst. Our tests took place at atmospheric pressure and at limited power. The reactor was not thermally insulated. The stationary and mobile electrodes are made of stainless steel; no post-plasma compartments.

Table 7

Test		61	62	71	72
Incoming flow l(n)/h	CO	19	9.7	-	-
	H ₂ O	9.4	9.4	-	-
	CO ₂	-	-	6.2	6.2
	H ₂	-	-	20	10
SE, kWh/m ³ (n)		1.3	2.1	1.4	2.4
Temperature °C	entry	195	200	26	26
	exit	320	320	310	315
Exit l(n)/kWh	H ₂	128	134	-	-
	CO	-	-	99	99
% Conv. of C		20	31	60	62

Thus, we demonstrate the feasibility of either non-catalytic conversion operation assisted by GlidArc-II plasma. Thereby, we open a new method of conversion of the carbon matter which can be applied to improve the composition of synthesis gases, pyrolytic gases or gases originating from gasification of waste and various industrial releases, knowing that these gases contain poisoning molecules for catalysts. Therefore, conversion of these gases into a SG of the required quality for the FT process opens the industrial possibility of conversion of waste into very pure synthetic fuel.

It is obvious that the direct or inverse shift assisted by the discharges generated in GlidArc-II can also serve for the production of Hydrogen starting from CO or of CO starting from Hydrogen.

Other Remarks and Conclusions

Our experiments have demonstrated the feasibility of a new process for the production of gases rich in hydrogen and carbon oxide, containing also very large quantities of C₂H₄ and C₂H₂. The process consists of producing these gases by means of the mobile electric discharges which strike directly in the light or heavy hydrocarbons mixed with water vapor and/or with carbon dioxide and/or with oxygen in any proportions. This causes oxidation and/or partial cracking of these hydrocarbons, avoiding the problems of the existing processes. The reagents, partially converted in a mobile discharge compartment, can then penetrate another post-plasma compartment near the direct reaction zone (plasma zone). There, in the presence of still active species, produced in the discharges and carried by the gas leaving the discharge zone, this gas undergoes an additional conversion at a slightly lower temperature than that present in the direct reaction zone.

The subject of this application is then a process which makes oxidation and partial cracking of hydrocarbons possible, in the active presence of water vapor and/or of carbon dioxide and/or of oxygen, without need for the intervention of other reagents or catalysts, as well as without the formation of soot, coke or tar which would hinder the proper operation of the reactor. The tests demonstrate clearly the feasibility of steam reforming, "dry" reforming with carbon dioxide, simultaneous reforming with an H₂O/CO₂ mixture or partial oxidation with oxygen, all accompanied by hydrocarbon non-catalytic cracking. This partial oxidation and steam reforming are also accompanied by reforming with carbon dioxide (if it is already present in the NG or is created by the over-oxidation parasite reactions).

Comparing Tables 1 through 6, we see that it is possible to oxidize or pyrolyze totally or partially a NG with reagents and/or diluent gases such as O₂, CO₂, H₂O, N₂ and H₂. These conversions take place in a very broad range of concentrations, with or without the presence of metal or ceramic matter initially non-catalytic in the zone near the

mobile discharge. The result of this is the production of a synthesis gas or of Hydrogen more or less accompanied by ethylene and acetylene without (or nearly without) soot. A free choice of the solid matter placed in contact with the post-plasma flow and a free choice of its temperature offer vast possibilities of orienting the composition of the product according to need, depending on the composition of the hydrocarbon feed, the availability of oxygen, etc.

5 Thus, injecting more or less electric energy directly into the discharges (see the SE values), we can convert more or less HC. For example, we can opt for a natural gas, seeded with hydrogen and carbon monoxide, for better combustion in piston engines or for transporting it through a traditional gas pipeline, to a civilized location where the CO and/or the H₂ would be extracted for a more sophisticated use. We can also convert the entire hydrocarbon feed and then send to a FT synthesis of a synthetic liquid HC. Everything indicates that a combination of the auto-thermal 10 process with mobile electric discharges provides a new approach to products of greater interest (presence of ethylene and acetylene), obtained starting from light or heavy HC feeds, partially oxidized by oxygen or by O₂-enriched air or by atmospheric air, all under low pressure of less than 6 bars.

On a more technical level, the amazing ease of operation of the reactor and of its assembly, without deterioration of electrodes, electrode holders, zone separators and all the reactor walls must be emphasized, since all 15 these components are subjected to the action of incoming reagents and outgoing products. This is explained by the moderate temperature of the assembly (< 1150°C) and by a very short contact time of the roots of the discharges with the stationary or mobile electrodes, even made of steel and even not cooled. We add that we never changed the steel or Ni electrodes or the Ni chips in the post-plasma zone; they underwent severe temperature and pressure conditions; they have "seen" the HCs, the O₂, the H₂O and other gases and vapors, they have worked covered by a layer of soot 20 at the time of some tests with very weak oxidizer/HC; they have been exposed then to an air or pure oxygen or CO₂ plasma...; it is clear that their activity does not depend on pre-treatment. They become active whenever they are exposed to the residual flow of species from the plasma zone.

Other positive points may also be mentioned for future practical application:

- The energy cost of treatment of the gaseous or liquid matter in GlidArc-II reactors does not appear to be high.
- We note the absence of any catalyst except that generated spontaneously by the electric discharge in the gas phase or on the surface of initially inert bodies placed in contact with the gas flow leaving the mobile discharge.
- The necessary reagents are extremely simple: water and/or CO₂ and/or O₂.
- The unit is very compact and, therefore, can be transported and installed near the storage, emission or extraction site of the products to be treated (for example, offshore oil platforms to convert associated gases).
- The process does not depend on the chemical; composition or purity of the gases or liquids to be treated.
- With the exception of the use of atmospheric or enriched air and of conversion of NG initially rich in CO₂ and/or N₂, the products exiting, after condensation of the water vapor, include very little CO₂ and no other foreign ballast increasing their volume, which makes the conversion and/or recycling operations easier.
- The GlidArc-II reactors have no thermal inertia and, therefore, can respond very quickly to control signals.

Extrapolation to large volumes will be easy.

Even with a non-optimized reactor, a great part of the initial molecules is converted into synthesis gas and into unsaturated hydrocarbons. This conversion is greatly improved by a subsequent passage of the reagents in the zone of discharges stratified in several zones. It will certainly be possible to improve these results by increasing the power of
5 the reactor. Since the GlidArc-II does not require any cooling, it can accept a gas arriving from high preheating, such as solar heat, which should reduce the electric demand of the process. It will then be possible to present our electrolysis in gaseous phase as a "cold" electric discharge developing in a hot gas.

While the present invention has been described with reference to particular embodiments, it will be understood that the embodiments are illustrated and that the invention scope is not so limited. Any variations,
10 modifications, additions and improvements to the embodiments described are possible. These variations, modifications, additions and improvements may fall within the scope of the invention as detailed within the following claims.

WHAT IS CLAIMED IS:

1. A process comprising:
 - providing one or more repetitive discharges between two or more electrodes, wherein at least one of said
5 two or more electrodes is mobile;
 - moving said at least one mobile electrode to stretch said discharges and place said discharges off thermal equilibrium; and
 - subjecting a flow of carbon substance to said discharges to promote chemical conversion of said carbon substance.
- 10 2. The process of claim 1 wherein subjecting said flow of carbon substance to said discharges is performed at a pressure of between 0.1 and 6 bars and at a maximum temperature of 1150°C.
- 15 3. The process of claim 1 wherein said carbon substance comprises heavy hydrocarbons and wherein said conversion comprises at least partial cracking of said heavy hydrocarbons into lighter carbon compounds.
4. The process of claim 1 wherein said carbon substance comprises heavy hydrocarbons and wherein said conversion comprises at least partial oxidation of said heavy hydrocarbons into lighter carbon compounds.
- 20 5. The process of claim 1 further comprising combining said carbon substance with an oxidizer, wherein said chemical conversion comprises reforming said carbon substance into a synthesis gas containing hydrogen H₂, carbon monoxide CO, and unsaturated hydrocarbons.
- 25 6. The process of claim 1 wherein said carbon substance comprises carbon dioxide CO₂, wherein the process further comprises combining said carbon substance with a hydrogen-containing substance, wherein said chemical conversion produces carbon monoxide CO.
7. The process of claim 1 wherein said chemical conversion produces less than 5% soot or coke, expressed in mass of carbon converted.
- 30 8. The process of claim 1 wherein said carbon substance comprises saturated hydrocarbons, and wherein said chemical conversion is achieved by pyrolysis of said hydrocarbons.
9. The process of claim 8 wherein said chemical conversion includes pyrolysis of one or more additional substances selected from the group consisting of unsaturated hydrocarbons, soot, and hydrogen H₂, wherein said one or more additional substances are generated by said pyrolysis.
- 35 10. The process of claim 1 wherein said chemical conversion is carried out in the presence of a metal or ceramic body located near said discharges, said body having a temperature of less than or equal to 1150°C, wherein said body catalyzes said chemical conversion.

11. A device for conversion of carbon substances comprising:
a plasma compartment configured to allow gasses to pass therethrough; and
an arc structure located within said plasma compartment, wherein said arc structure includes a first
electrode and a second electrode which is movable with respect to said first electrode, wherein
5 an electrical discharge between said first and second electrodes creates an off-equilibrium
plasma.
12. The device of claim 11 wherein said second electrode is selected from the group consisting of: a toothed
disk; a disk having a smooth edge; and a disk having a brush around its circumference.
- 10 13. The device of claim 11 further comprising an electric generator coupled to said first and second
electrodes.
14. The device of claim 13 wherein said generator comprises a multi-phase generator and wherein one pole
15 of said generator is coupled to said first electrode and a neutral point of said generator is coupled to said second
electrode.
16. The device of claim 13 wherein said generator comprises a plurality of monophase generators and
wherein one pole of each of said plurality of monophase generators is coupled to said first electrode and another
20 pole of each of said plurality of monophase generators is coupled to said second electrode.
17. The device of claim 11 further comprising a solid material located in close proximity to said electrodes.
- 25 18. The device of claim 17 further comprising a maturation compartment in fluid communication with said
plasma compartment, wherein gasses pass through said plasma compartment and into said maturation
compartment.
19. A method comprising:
providing a reactor having an arc compartment, said arc compartment having two or more electrodes
wherein at least one of said electrodes is mobile;
introducing a mixture in gaseous form into said arc compartment, wherein said mixture comprises a
30 carbon-containing substance;
providing one or more electrical discharges between said mobile electrode and another of said electrodes
to create an off-equilibrium plasma; and
submitting said mixture to said off-equilibrium plasma to convert at least a portion of said mixture into a
synthesis gas.

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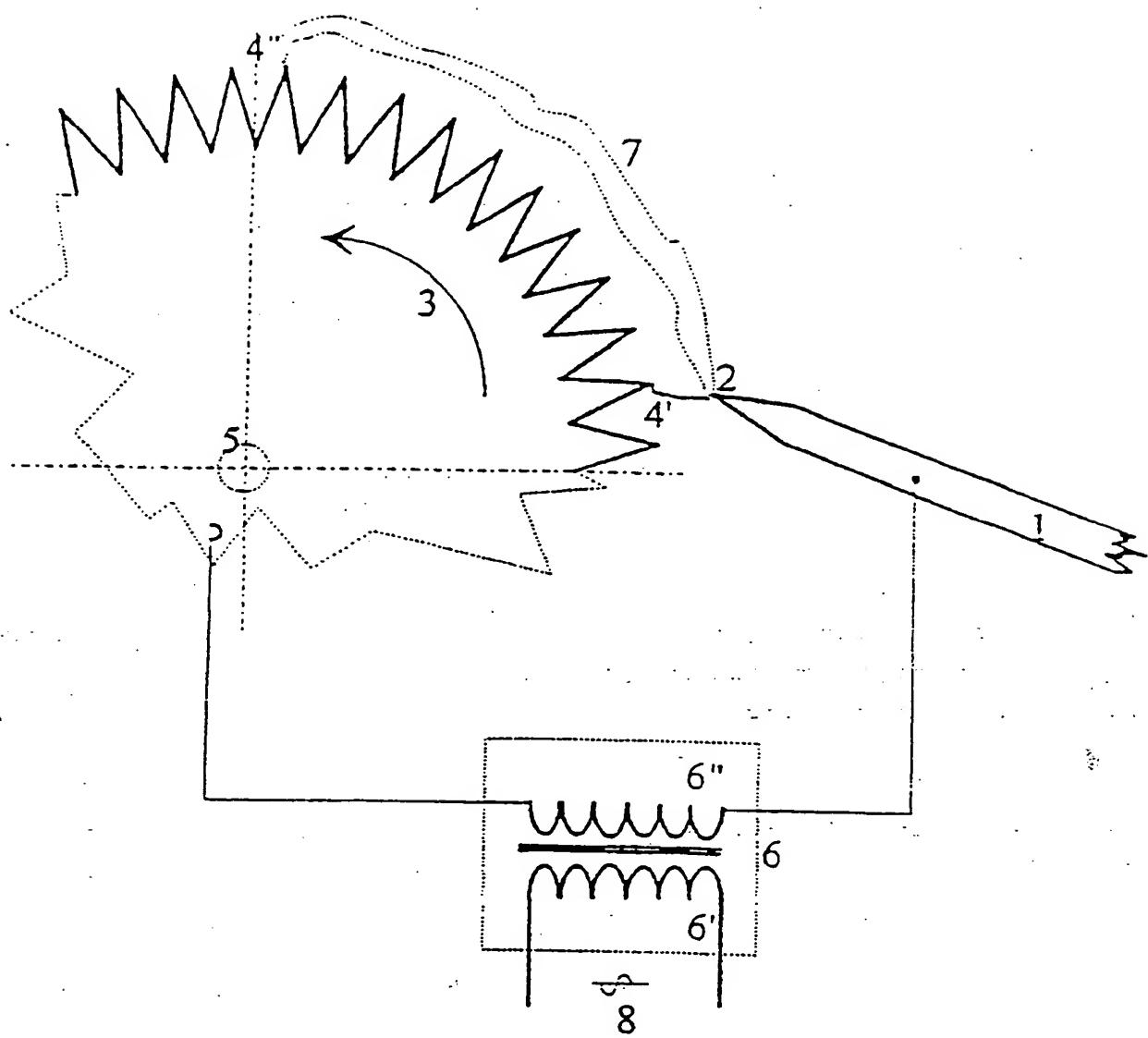


Fig. 1

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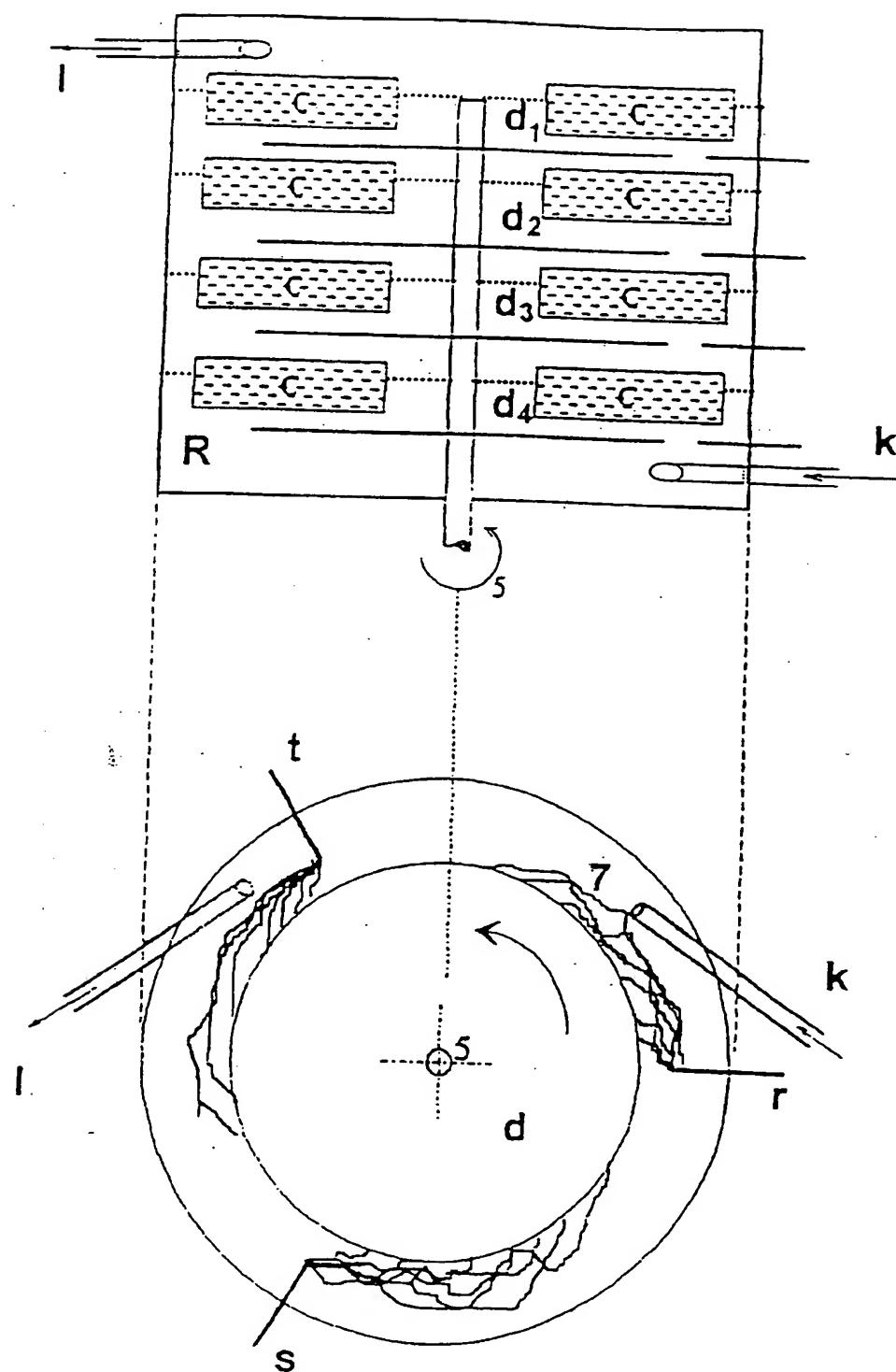


Fig. 2

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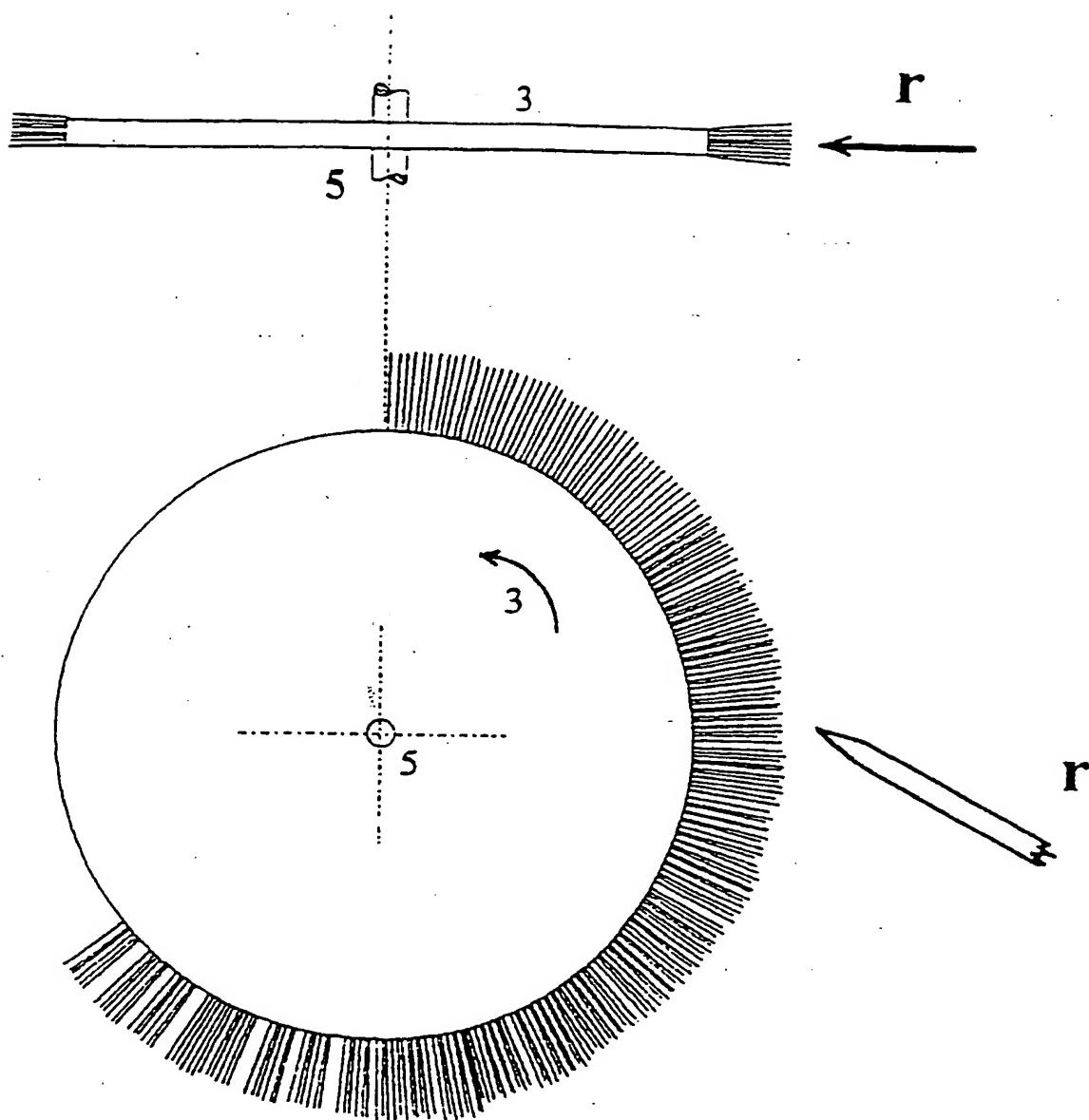


Fig. 3

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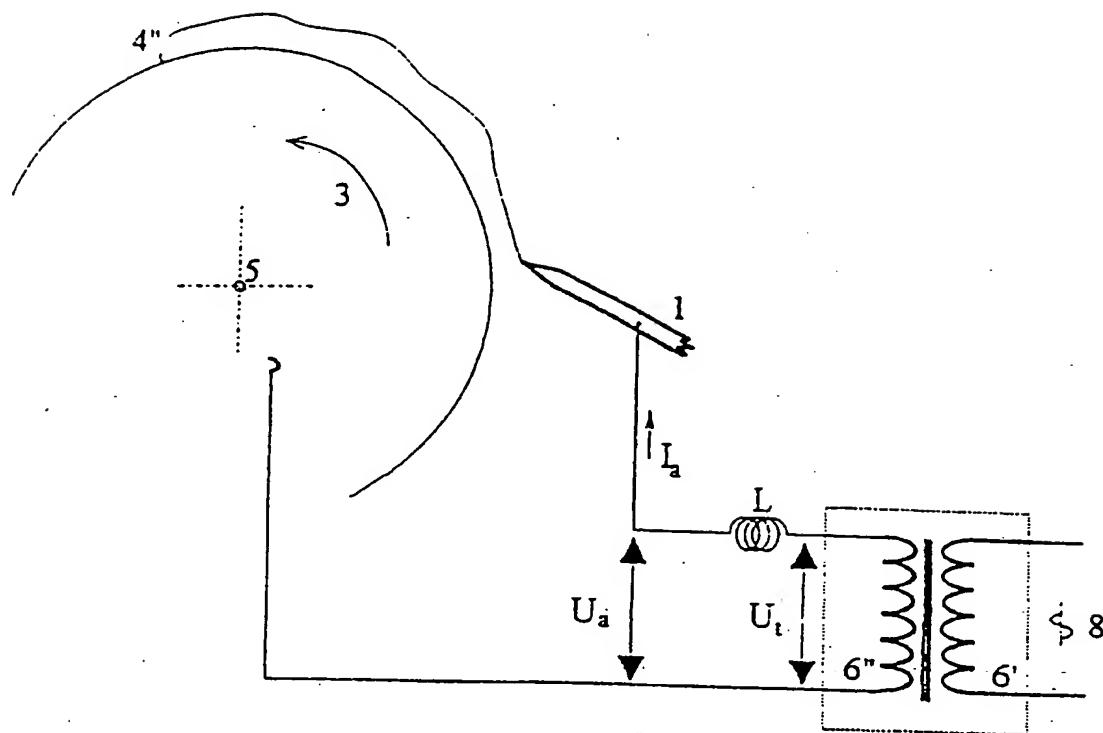


Fig. 4a

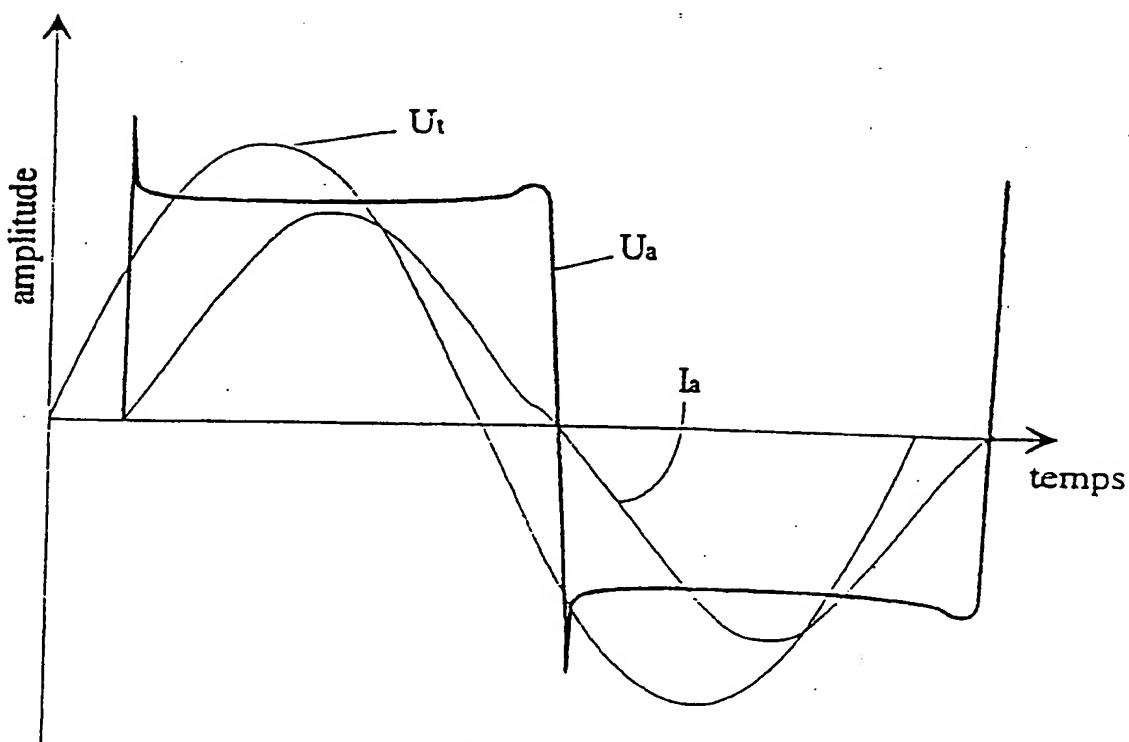


Fig. 4b

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/20204

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 801J19/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 801J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 3, line 51 -page 4, line 27	1-10, 19
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	page 7, line 51 -page 11, line 60	
	figures 1,7-9,15-22	
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	-/-	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means.</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>		
<p>"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search		Date of mailing of the international search report
11 February 2000		21/02/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer Vlassis, M

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Y	FR 2 758 317 A (CZERNICHOWSKI PIOTR) 17 July 1998 (1998-07-17) cited in the application the whole document ----	1-10,19

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